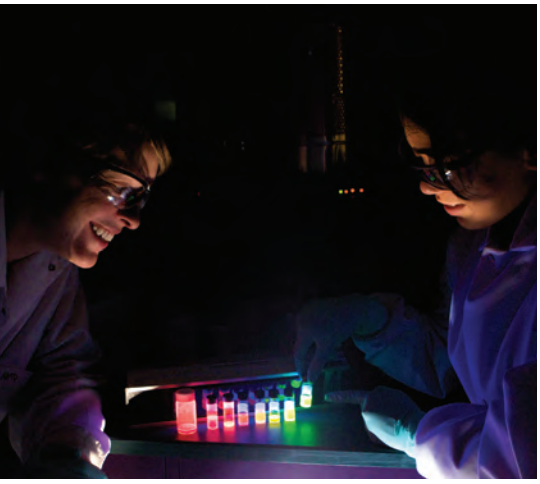
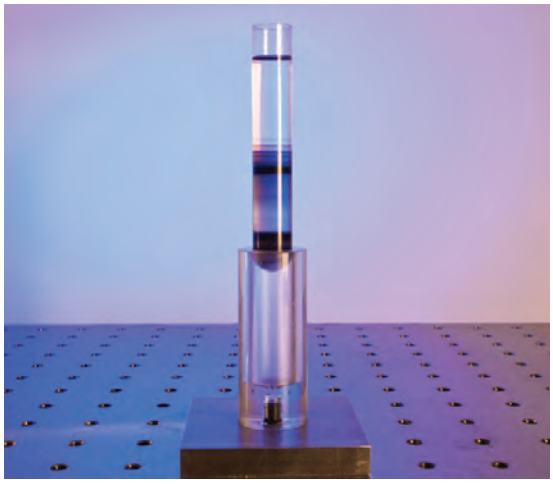
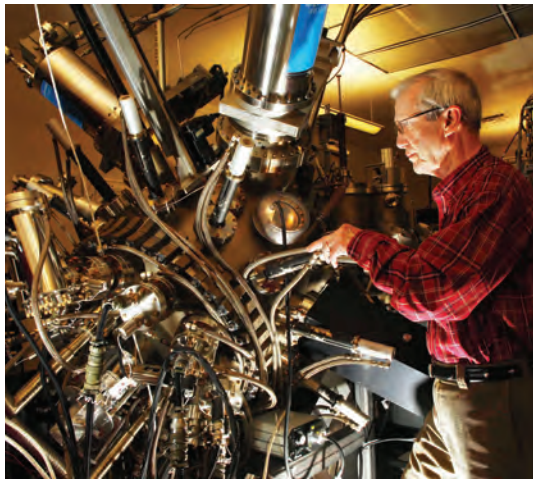
The Center for Integrated Nanotechnologies







2010
Annual Report

Center for Integrated Nanotechnologies

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From the Directors' Office

David Morris, Director

Jeff Nelson, Acting Co-Director

Tom Picraux, Chief Scientist

Neal Shinn, User Program and Ourreach Manager

We are pleased to present this 2010 Annual Report from the Center for Integrated Nanotechnologies. This has been a very exciting and eventful year for our Center highlighted by our triennial facility operations and science review by the Department of Energy and a very successful Annual User Conference. There have been a number of transitions within both management and staff ranks this year as our colleagues have assumed exciting new challenges within our host Laboratories and in the academic community. We are pleased to be welcoming new members into our Center who represent new capabilities and experience from which we are already reaping benefit. A brief introduction to our new CINT Scientists is provided herein (p. 6). The main focus of our Center continues to be our user program, and we were pleased to host 358 users in the 2010 reporting period representing 355 active project proposals.

Our vision for nanoscience integration continues to inform the growth and strategic evolution of our science program. We are pleased to note that our new Integration Focus Activity initiative rolled out last year has really taken root. Our initial focus activities were in Nanowires for New Energy Concepts and Membrane-based Nanocomposites. We have added a third focus in the area of Metamaterials and Plasmonics. These efforts (p. 12) unite our scientists across our four Thrust areas with our users to concentrate research on larger-scale nanoscience integration challenges for specific classes of materials, systems, and phenomena. Our Discovery Platform initiative has also seen exciting growth this year (p. 13) with design updates to add new functionality to an existing platform and entirely new platforms to support our focus on nanowire characterization and integration.

To better serve our User community we have made two notable operational adjustments this year. The first is to transition to a new more versatile and user-friendly proposal submission and tracking database, and the second is to establish a proposal submission and review calendar with fixed dates. We are grateful to our colleagues at the Molecular Foundry for providing us with their database shell around which we are developing a customized CINT system. Our new proposal calendar will retain two calls per year, and users can now anticipate fixed calls on March 1 and September 1 each year.

The program for our annual User Conference (p. 17) was again organized around mini-symposia on topics of current high levels of interest within our Center and the community. In addition, we added a new special session on the opening night directed at outreach to industrial users. This session was a resounding success and reflects our eagerness to enhance industrial access to our Center. We also sponsored a Nanoscale Science Research Center-wide workshop on theory and simulation in nanoscale materials and participated in a similar workshop sponsored by our colleagues at the Center for Nanoscale Materials at Argonne National Laboratory (p. 21). These workshops drew excellent reviews from the participants and reflect an increasing effort to build a broader sense of community within the family of NSRCs.

Finally, we would like to acknowledge with gratitude our Science Advisory Committee and Governance Board, our User Executive Committee, and the host of users who made invaluable contributions in helping us to prepare for and successfully execute our triennial DOE on-site review. This was genuinely a community effort for which we can all take pride. We welcome feedback and invite suggestions from our users and all stakeholders on all aspects of our user program and Center operations. We hope you find this annual report informative and, more importantly, that it will motivate you to join us as a new user or continue your engagement with CINT.

We dedicate this 2010 edition of the CINT Annual Report to the memory of Professor Paul F. Barbara, Richard J. V. Johnson – Welch Regents Chair in Chemistry in the Department of Chemistry and Biochemistry at the University of Texas, Austin. Paul was a true pioneer in this exciting enterprise of nanoscience, and his friendship, sage advice, and tireless support of CINT as member and chair of our Science Advisory Committee were vital to pointing us along and keeping us on a path to success.

About CINT

The Center for Integrated Nanotechnologies (CINT) is a Department of Energy/Office of Science Nanoscale Science Research Center (NSRC) operating as a national user facility devoted to establishing the scientific principles that govern the design, performance, and integration of nanoscale materials. Jointly operated by Los Alamos and Sandia National Laboratories, CINT explores the continuum from scientific discovery to use-inspired research, with a focus on the integration of nanoscale materials and structures to achieve new properties and performance and their incorporation into the micro- and macro worlds. Through its Core Facility at Sandia National Laboratories and its Gateway Facility at Los Alamos National Laboratory, CINT provides open access to tools and expertise needed to explore the continuum from scientific discovery to the integration of nanostructures into the micro- and macro worlds. In its overall operations, CINT strives to achieve the following goals common to all Nanoscale Science Research Centers:

1. Conduct forefront research in nanoscale science;
2. Operate as a user facility for scientific research;
3. Provide user access to the relevant BES-supported expertise and capabilities at the host national laboratory;
4. Leverage other relevant national laboratory capabilities to enhance scientific opportunities for the nanoscience user community;

These additional goals are specific to the unique CINT mission:

5. Establish and lead a scientific community dedicated to solving nanoscale science integration challenges;
6. Create a single user facility program that combines expertise and facilities at both Los Alamos and Sandia National Laboratories.

The CINT user program provides the international scientific community with open access to world-class scientific staff and state-of-the-art facilities for theory and simulation, nanomaterials synthesis and characterization, and unique capabilities for nanoscale materials integration, from the level of nanoscale synthesis to the fabrication of micro- and macroscale structures and devices. The staff of CINT includes laboratory scientists, postdocs and technical support staff who are leaders in the nanoscience research programs in CINT scientific thrust areas:

Nanoscale Electronics and Mechanics,
Nanophotonics and Optical Nanomaterials,
Soft, Biological and Composite Nanomaterials, and
Theory and Simulation of Nanoscale Phenomena.

The thrusts have been developed over the past several years by engaging the broader scientific community through discussions with potential CINT users and with attendees at CINT workshops, as well as by attracting some of today's top nanoscience talent to become CINT staff.

New CINT Staff

Quanxi Jia

Quanxi officially joined CINT in December 2009, as the Leader for the Nanoscale Electronics and Mechanics Thrust based at the Gateway.

Quanxi's research interests have focused on the growth of metal-oxide films, the study of processing-structure-property relationship of electronic materials, the monolithic integration of metal-oxide materials with complimentary functionalities for novel devices, the fabrication of electronic devices, and the structural/electrical characterization of electronic materials. His recent work covers the investigation of energy storage/conversion materials and multifunctional nanocomposites including ferroelectric, ferromagnetic, multiferroic, and high-temperature superconducting materials

Nathan Mara

Nate joined CINT in March 2010 as a scientist in the Nanoscale Electronics and Mechanics Thrust at the Gateway.

His research includes:

- Nanomechanical behavior of nanocomposites, metals, ceramics, intermetallics, and metallic glasses
- Bulk synthesis of structural nanomaterials
- Microstructural characterization of materials via Electron Microscopy (SEM, TEM, HRTEM, STEM, in-situ techniques)
- Development of novel mechanical testing techniques

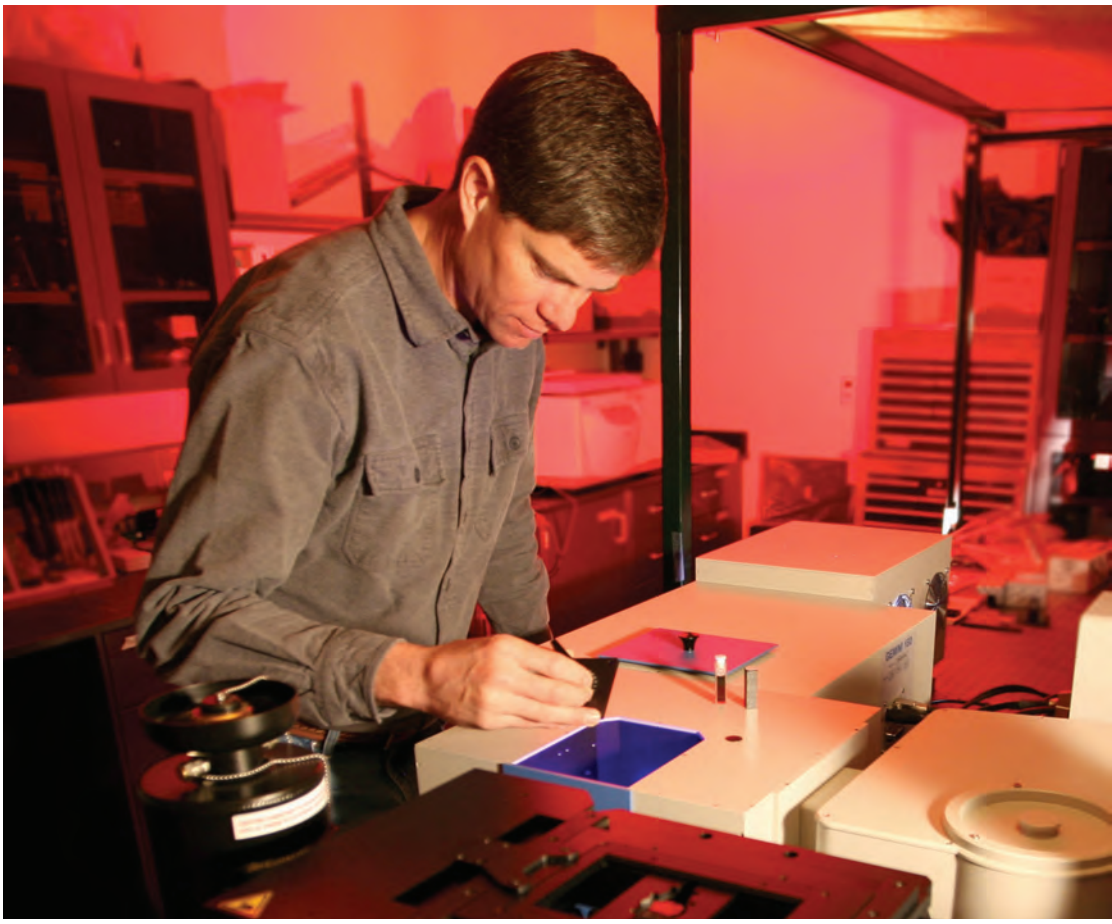
New Staff Highlight - Steve Doorn

Bringing carbon nanomaterials and plasmonic nanoparticles expertise to CINT

Stephen Doorn has always admired the capabilities of the Center for Integrated Nanotechnologies (MPA-CINT). So when the chance to lead the Los Alamos nanophotonics and optical nanomaterials thrust became available, Doorn pursued it—and got it. "It's an exciting opportunity for me," said Doorn, who has collaborated with CINT scientists throughout his time at Los Alamos National Laboratory (LANL). "There are a lot of great capabilities at CINT that I am stepping into. With the research that I do, this move is a great fit for me."

Doorn, who has a PhD from Northwestern University in physical chemistry, began his Laboratory career 20 years ago as a postdoctoral fellow. Previously with the Physical Chemistry and Applied Spectroscopy group at LANL, Doorn joined CINT in February, leading a team of postdoctoral researchers and staff studying plasmonic nanoparticles and carbon nanotubes. In his new role, he assists in expanding the CINT user program, while helping to coordinate collaborative efforts between the CINT facilities at Los Alamos and Sandia National Laboratories.

"He brings a brand new set of capabilities," CINT Director David Morris said. "He is internationally recognized in his field. He has a strong background in carbon nanotube materials and spectroscopy research, which he is parlaying into new applications. He has a lot of experience at the Laboratory and he has demonstrated that he is a really successful leader. That is what we were looking for."



Doorn's primary research interests include studying fundamental behaviors along with applications of carbon nanomaterials and plasmonic nanoparticles. By studying the fundamental electronic and optical behavior of carbon nanotubes, which Doorn described as supplying "a continuing stream of interesting and exciting challenges," he hopes to create samples that can be used in experiments aimed at potential applications in both chemical and biological sensing and imaging.

Doorn's plasmonic nanoparticles research aims to develop gold and silver nanoparticles as bright spectral tags with unique signatures (or fingerprints) using what is known as the surface enhanced Raman (SERS) effect for applications in rapid flow-based bioanalytical applications. The challenge in these applications has been to increase the degree to which multiple chemicals may be detected and identified simultaneously, a process called multiplexing.
"The SERS tags provide a variety of bright and easily identified fingerprints, providing a path to advanced multiplexing in sensing applications," Doorn said. "Because of this they are gaining interest for bioassay and imaging needs."

Doorn and scientists in the Bioscience and Chemistry Divisions at LANL recently advanced the state of this research with the development of a full-spectral in-flow Raman instrument that fully utilizes the SERS-tag signatures in multiplexed assays. The new instrument is seen as a powerful new tool for nanomaterials development and is envisioned to take on an expanded role in characterization and development of several nanoparticle types, including quantum dots, nanowires, and carbon nanotubes. (For details, see "High-Resolution Spectral Analysis of Individual SERS-Active Nanoparticles in Flow," J. Am. Chem. Soc. 132 (17), 6081 [2010]).

Doorn's scientific expertise is demonstrated not only in the lab, but also appreciated by younger scientists. He is a recipient of a 2008 Department of Energy Office of Science Outstanding Mentor Award and mentors numerous postdoctoral researchers. Nathan Mack (C-PCS), who was Doorn's postdoctoral researcher for four years, described Doorn as "a great mentor, allowing us space to develop new projects and ideas. He is very attentive and was always there whenever we had a problem. He is very knowledgeable. CINT is lucky to have such a talented individual."

Hou-Tong Chen

Hou-Tong became a CINT Scientist at the Gateway in June 2010. He is with the Nanophotonics and Optical Nanomaterials Thrust.

Hou-Tong's research at CINT focuses on metamaterials and surface plasmonics, mainly in the terahertz frequency range. These involve the design, numerical simulation, fabrication, and characterization of passive, dynamical, and active metamaterial and surface plasmonic devices. His recent activities include dynamical and active hybrid metamaterials, metamaterial antireflection, and superconducting metamaterials, as well as investigating the underlying physics. He is also interested in terahertz time domain spectroscopy and ultrafast laser spectroscopy for material and device characterizations.

Walter Paxton

Wally is the newest member of the CINT Scientist community, joining us in December 2010. He is based at the Core facility in the Soft and Biological Nanomaterials Thrust.

Wally's research focuses on the integration of natural and synthetic functional molecules into biomimetic materials at interfaces. He is developing new strategies for efficient integration of functional molecules, including transmembrane transport proteins, and the means to characterize the action of these exotic molecules at interfaces. This work involves (1) the chemical functionalization of solid supports by a variety of means including soft lithography and scanning probe lithography, (2) the synthesis of small organic molecules and monomers, and (3) the preparation, characterization, and modification of amphiphilic block copolymers.

New Capabilities & Instrumentation

Computer Cluster

A 100-node computer cluster has been installed featuring modern architecture (8CPU/32Gb memory per node) and utilizing fast interconnect technology for parallel computations. The new cluster allow us to increase our computational power by a factor of 10, memory capacity by a factor of 5, and storage capacity by a factor of 10. Furthermore, fast interconnect capabilities will make it possible to run medium/large scalecomputational tasks in parallel. (Contact Sergei Tretiak)

Near-IR fluorescence imaging and spectroscopy

This system offers both single-line laser and broad wavelength-selectable lamp excitation for fluorescence and photoluminescence excitation spectroscopy on solution and solid bulk samples. The spectroscopy is integrated to a microscope, which allows confocal fluorescence imaging and spectroscopy on single nanostructures. The microscope is paired with a 2-D InGaAs imaging array to allow wide-area direct imaging of individual nanostructures and assemblies in real-time. (Contact Steve Doorn)

Multi-Photon Laser Scanning Confocal and Fluorescence Lifetime Imaging Microscope

This instrument consists of Multi-Photon Laser Scanning Confocal Microscope (Olympus FV1000) with a Fluorescence Lifetime Imaging Attachment (Lambert Instruments). It is among the most advanced, commercially available optical imaging systems, and gives CINT a world-class capability for optical characterization of any array of biological, synthetic, and hybrid nanomaterials. Techniques enabled by this system include Fluorescence Recovery After Photobleaching (FRAP), Fluorescence Resonance Energy Transfer (FRET), Total Internal Reflectance Fluorescence (TIRF). The FLIA module will enable spatial mapping of fluorescence lifetimes. (Contact Gabriel Montano)

IR Variable angle spectral ellipsometer

An infrared variable angle spectral ellipsometer has been installed at the core CINT facility. The instrument is an IR-VASE from J.A. Woollam and covers a spectral range from 2 to 40um. The instrument allows optical characterization of thin films and substrates in this spectral range, for example refractive index (n) and extinction (k) coefficients. These experimentally determined optical parameters can then be used for the design of complex optical devices such as metamaterials, dielectric stacks, etc. (Contact Igal Brener)

AFM Imaging

An Asylum MFP-3D-SA AFM system allows for both standard and user-defined operation modes. A specific application focus of this new AFM is imaging and spectroscopic force measurements of dynamic biological and biomimetic assemblies and structure formation. (Contact Gabriel Montano)

High-Resolution X-Ray Diffraction System

The XRD instrument is comprised of a high-precision XRD platform with small-angle x-ray scattering, and variable temperature/pressure, thin-film, and microdiffraction accessories. It is capable of variable-temperature and pressure crystal phase identification and quantification; size, size-distribution and shape analysis of nanocrystals and crystalline domains; film thickness in single and multilayer films together with core and shell thickness determination in heterogeneous core/shell nanocrystals; stress analysis in films and heterogeneous nanomaterials; and quality control of epitaxial films and superlattices. (Contact John Reno)

Atomic Layer Deposition System

This state-of-the-art atomic layer deposition (ALD) system, housed in our Integration Lab, utilizes precursor gases with single atomic layer control to enable conformal coating for nanoscale structure integration. ALD offers a unique means for the conformal deposition of dielectric and metallic films on 3-dimensional nanostructures with single atomic layer control. (Contact John Nogan)

DC Sputtering/Thermal Evaporation System

The new AJA International, Inc. ATC Orion Series Combination DC Sputtering/Thermal Evaporation System provides ease-of-use and operating flexibility. The magnetron sputtering sources feature a modular magnet array that allows operation in a variety of modes depending on our particular application for a specific film deposition run. The system also allows for "confocal sputtering," which provides rapid sputtering of high quality and uniformly thick metal films (+/- 2.5% thickness uniformity over 4" diameter substrates). The unique isolation chimney prevents cross-contamination of target materials and allows deposition profiles to be fine-tuned, allowing sequential deposition of a series of metals (2-4) in single runs (without breaking vacuum). (Contact Jennifer Hollingsworth)

Low-Pressure Chemical Vapor Deposition

A low pressure chemical vapor deposition (LPCVD) / diffusion furnace has been installed in our Integration Lab for deposition of high quality low stress films including LPCVD SiN, thermal SiO2, LPCVD SIO2, and LPCVD Poly-Si layers for electrical isolation and for mechanical support. Mechanical support allows for high density films (e.g. low imperfections) without significant stresses. For micro-electromechanical systems (MEMS) and nano-electromechanical systems (NEMS) the ability to tailor the stress is key as stress and stress gradients are dominant mechanisms that induce device failure. (Contact John Nogan)

Ultrafast Laser System for Rapid Prototyping

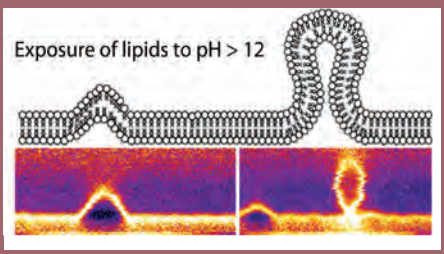
We have developed a turnkey, ultrafast laser system for rapid prototyping devices including 2D microfluidics and 3D waveguides in bulk media. The system can also perform multi-photon processing of polymers, surface texturing, and patterning of arbitrary 2D array structures, such as thin film metamaterials, onto a substrate. Feature sizes are user definable and currently range from hundreds of nanometers to <10um. (Contact Quinn McCulloch)

Graphene Reactor

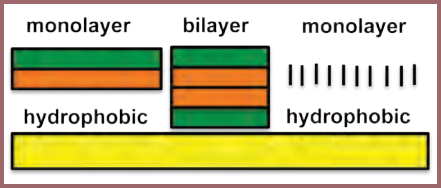
We have developed a large area graphene growth capability at CINT that allows us to make graphene samples available to CINT users. The graphene is grown on copper foil by a chemical vapor deposition process using either liquid or gas precursors. We have also developed the techniques to transfer the large pieces of graphene to virtually any substrate for further characterization. (Contact Andrew Dattelbaum)

Visit our website for additional details on all these new capabilities.

Membrane-Based Nanocomposites



Confocal microscopy images (bottom) reveal that disrupting the interactions between a supported lipid bilayer and the substrate can trigger the nucleation, growth, and launching of cell-like vesicles into the overlying solution.

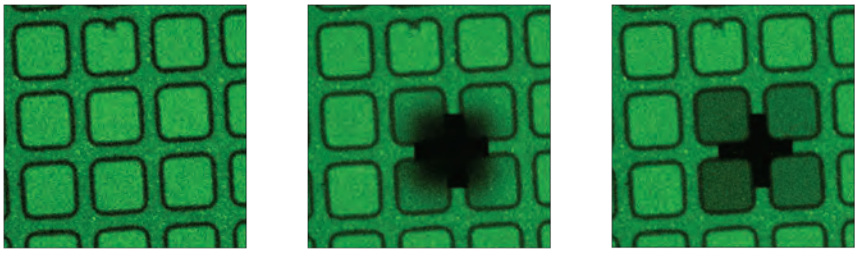


Depiction of a cross-section of how adsorbed polymersomes organize into ordered layers on patterned substrate surfaces. The hydrophilic substrate (yellow) is covered with square patches of a hydrophobic monolayer (red). The polymersome contains both hydrophobic (orange) and hydrophilic (green) blocks. The polymersome adsorbs from solution such that the hydrophobic squares interact with the hydrophobic blocks to form a monolayer, while the hydrophilic substrate interacts with the hydrophilic blocks to create an adsorbed polymersome bilayer.

The focus of the Membrane-Based Nanocomposites Focus Area is to explore the extent to which nanoparticles and other nanomaterials can be manipulated when integrated into fluid and responsive hosts such as lipid bilayers. The ultimate goals of the research involve learning how to replicate many of the complex behaviors associated with cellular membranes within artificial nanocomposites and integrated systems. These integrated nanomaterials could be utilized in applications including electrical energy storage (the artificial electric eel), artificial photosynthesis, environmental remediation (reversible CO2 sequestration and water purification), and responsive sensors and adaptive materials for Homeland Defense applications.

The starting point for understanding the behavior of complex membranes involves understanding the fundamental interactions between fluid hosts, nanoparticles, and substrate surfaces. During the past year, our research has been directed at providing a scientific framework for predicting the behaviors associated with interactions involving lipid bilayers, including: 1) nanoparticle adsorption, insertion, migration, and aggregation as a function of particle size, shape, and surface chemistry, and 2) lipid responses as mediated by substrate interactions, including diffusion and transport, mechanical stability, domain formation and component partitioning, reversible ion channel formation, and transitions between various assembled geometries including supported lipid bilayers, cell-like vesicles, and hollow lipid nanotubes.

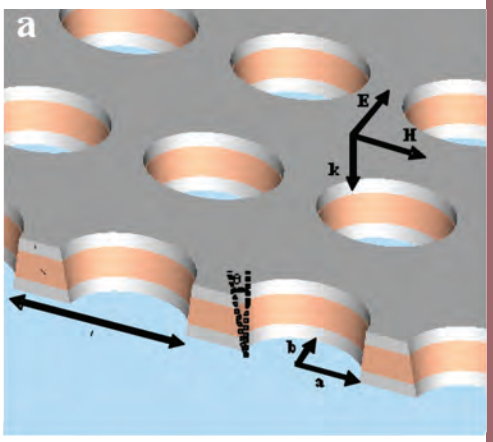
Most recently, we have begun to explore the behaviors exhibited by fluid hosts consisting of block copolymers. The copolymers of interest have hydrophilic and hydrophobic domains that self-assemble into cell-like vesicles called polymersomes. These polymersomes mimic many of the attributes of the lipid bilayers found in cellular membranes. Potential advantages of the polymersomes relative to traditional lipid bilayers include enhanced stability, as well as the ability to tune the thickness and chemistry of the bilayer to accommodate a wider range of nanoparticle sizes and compositions. We have also been exploring hybrid bilayers containing both polymersomes and lipids. For certain compositions, we have discovered that lipid molecules are free to migrate within a relatively immobile array of polymersome molecules, combining the responsiveness of a lipid bilayer with the stability of a polymersome within a composite host. In the coming year, we plan to start introducing molecular species into our nanoparticle-fluid host composites as a means of introducing reversible programming and responsive behavior into the composites.

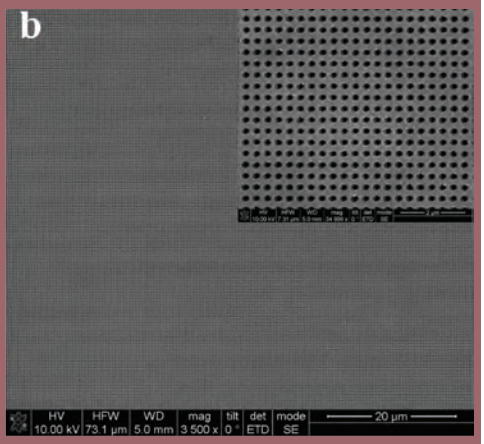


The top view of a photobleaching study conducted on photo-labeled polymersomes adsorbed on the patterned substrate (right). Photobleaching defines a dark square over both hydrophobic squares and hydrophilic interstices (center). Rapid recovery over the hydrophobic zones reveals that polymersomes in the overlying monolayer are highly mobile, while the total lack of recovery in the hydrophilic zones shows that the adsorbed bilayer is immobile. This result clearly shows the dramatic effects that surface patterning and chemistry can have on the structure and responsive properties of supported bilayer films.

Metamaterials and Plasmonics

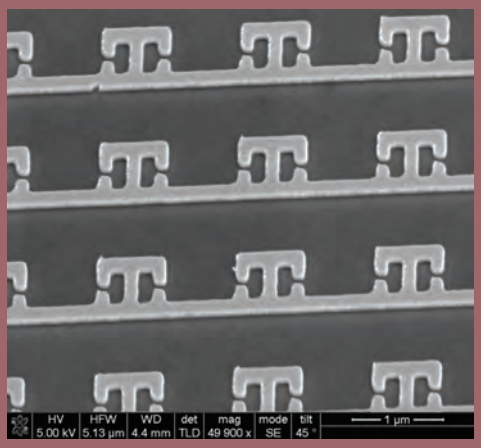
The Metamaterials and Plasmonics Integration Focus Activity builds upon the extensive activities at CINT over the past few years on active and passive metamaterials and plasmonic resonators. This field has blossomed in the research community with the realization that it is possible to create "artificial" electromagnetic composites that combine unusual magnetic and electric responses. This new class of electromagnetic materials greatly extends our ability to manipulate electromagnetic radiation, and has led to the demonstration of unique behavior such as negative refraction, cloaking, and superlensing. Our past activities in this area have led to groundbreaking work in planar terahertz metamaterials, their passive optical properties and their applications to sensing. Through their integration with doped epitaxial layers, CINT has been a leader in tunable metamaterials, both electrically and optically.





(a) Diagram and (b) top view SEM image of fabricated elliptical negative-index metamaterials. The structure is composed of a 60 nm amorphous Si layer sandwiched between two 28 nm Ag layers. The polarization and propagation direction is also depicted in (a).

Recent milestones in 2010 include the integration of metamaterials with high-temperature superconductors showing thermally and optically tunable resonance strength and frequency, the realization of antireflectors and perfect absorbers in the far infrared, the demonstration of tunable resonances in the mid-infrared through nanofabrication and the use of lower bandgap and higher mobility III-V semiconductors, and metamaterials that are used to alter Casimir forces at the nanoscale. In the area of plasmonics, we have a number of user projects that aim to use plasmonic resonances for chem-bio sensing, and novel fabrication techniques that lead to record field enhancement for spectroscopic applications such as Raman scattering.



Interconnected metamaterial resonators fabricated using e-beam writing and liftoff on a doped semiconductor substrate for electricaly tunable optical metamaterials in the thermal infrared.

Through a vibrant network of users and research groups at both National Labs, this Integration Focus Activity will continue its expansion into new directions such as active electrical tuning of metamaterials at smaller dimensions to achieve higher optical frequencies (mid and near infrared), the integration of metamaterial and plasmonic resonators with complex oxides and other epitaxial bandgap engineered heterostructures for possible nonlinear optical behavior, and strategies that aim at reducing intrinsic loss in metal based metamaterials through integration with nanomaterials that can provide compensating gain, such as quantum dots, nanowires and other heterostructures.

Nanowires for Energy Concepts

The novel properties of nanowires offer tremendous opportunities for transformative energy applications. These multi-purpose materials combine nanoscale and even quantum-confinement effects with enhanced transport properties. CINT scientists together with our user community are focusing to understand and control the functionality and integration of heterogeneous semiconducting nanowires for new energy harvesting and storage concepts. We emphasize heterogeneous nanowires to realize an unprecedented level of control over material performance by tuning interface, strain, and materials-mixing effects. We combine new synthesis strategies with structural, electrical, optical, and thermal characterization, initially at the single-nanowire level to answer critical science questions underlying new nanowire materials concepts for photovoltaics and thermoelectrics. We also drive toward functional integration of nanowires into two- and three-dimensional architectures.

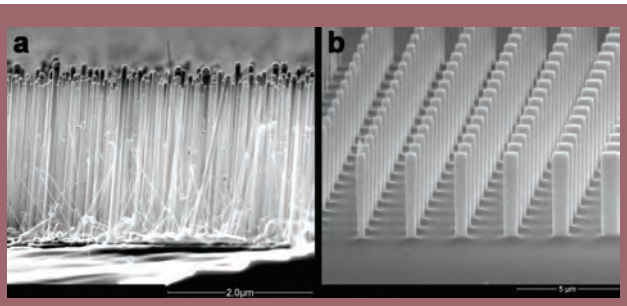


Figure 1. Bottom-up and top-down approaches to complex nanowire fabrication and array formation. (a) Vapor-liquid-solid grown Ge nanowire arrays toward hetero-Si/Ge nanowires possessing ultra-sharp interfaces. (b) Si nanowire array fabricated by electron beam patterning and plasma etching for subsequent radial p-n junction formation.

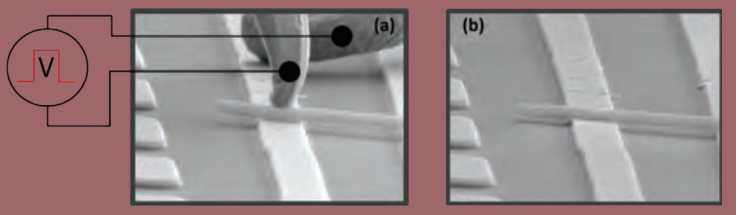


Figure 2. Spot welding of a SiGe-alloy nanowire on a lead of the thermoelectric characterization platform. (a) Before voltage pulse is applied. (b) After the voltage pulse the nanowire is embedded into the metal lead.

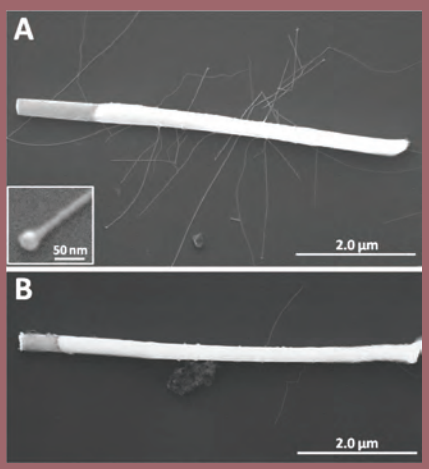


Figure 3. Hybrid semiconductor-metal nanowires. (a) Ni-Au nanorods with attached high-density CdSe nanowires. (inset) Close-up view of a CdSe nanowire with Bi-catalyst tip. (b) Ni-Au nanorods with attached low-density CdSe nanowires.

Selected Recent Highlights:

Nanowire heterostructuring bottom-up and top-down. High-density arrays of germanium nanowires were grown epitaxially along the <111> crystal direction by the bottom-up vapor-liquid-solid process (Figure 1a). These nanowires are part of a study to in situ alloy the gold growth seed with gallium (dark hemispheres at top of wire) to form extremely sharp Si/Ge axial heterostructured interfaces. Periodic arrays of silicon nanowires were also fabricated by a top-down process of electron beam patterning and plasma etching (Figure 1b). Here, radial p-n junction devices are subsequently grown on the nanowires, which are being studied for enhanced optical absorption and photovoltaic response for nanowire array solar cell applications.

Nano-welding. Resistance at the nanowire-contact interface is the bane of nanowire property characterization. Electrical contact resistance can overwhelm a 2-point intrinsic resistivity measurement, and thermal contact resistance leads to a temperature discontinuity that makes extraction of thermal properties difficult, if not intractable. We developed a nanowire spot-welding technique using the nanomanipulator that virtually eliminates contact resistance by melting the material at the nanowire-contact interface thereby forming a well-bonded interface contact (Figure 2). We used this method to attach individual SiGe-alloy nanowires to a CINT-developed thermoelectric characterization platform to measure the thermal and electrical conductivities, and the Seebeck coefficient, all on the same nanowire as a function of temperature. This was done on nanowires with different diameters and doping levels to extract the principal scattering mechanisms determining thermal transport.

Nanowires "wired-up." As an alternative approach to addressing the nanoscale "contact problem," we have developed a novel solution-based method to fabricate semiconductor NWs with built-in electrical contacts. We used templated electrochemical deposition methods to fabricate metal rods and nanowires, where choice of metal is flexible (e.g., Au, Ag, Cu) and magnetic segments can be added to facilitate separation and post-fabrication assembly using applied magnetic fields. We have successfully grown II-VI semiconductor nanowires from the metal nanostructures at controlled densities using a modified Solution-Liquid-Solid growth technique (Figure 3). Electrical conductivity measurements are currently underway.

Discovery Platforms

A Discovery Platform™ is a modular micro-laboratory designed and batch fabricated for the purpose of integrating nano and micro length scales to study the physical and chemical properties of nanoscale materials and devices. Discovery Platforms™ are standardized and packaged to allow easy connections with external electrical, optical, and fluidic devices. The design and packaging also allow access for a wide range of external diagnostic and characterization tools available at CINT.

Nanomechanics and Thermal Transport Discovery Platform (NMTTDP)

CINT's new 'Nanomechanics and Thermal Transport Discovery Platform' (NMTTDP), is being used by researchers for the study of the nanomechanical behavior of phase change memory materials and for the study of electrochemically-induced strain in energy storage materials. This new work takes advantage of additional design features that were developed and added to the previous Cantilever Array Discovery Platform. For example, in the CINT user work from Prof. Dan Gianola's group at U. Penn, "In Situ Mechanical Testing of Phase Change Nanowires Using the CINT Discovery Platform," the new nanomechanical test stages of the NMTTP were employed to measure changes in electrical properties simultaneous with mechanical property measurement for high performance phase change memory nanowires (GeSb and $Ge_2Sb_2Te_5$). The key feature on the NMTTP that enabled this work was the creation of nanomechanical test structures that have electrical leads on both sides of the mechanical stage. This required a novel floating electrical lead on a suspended spring (see Image 1). Preliminary data on the electrical and mechanical properties of suspended GeSbx nanowires (see Image 2) has been obtained. The goal of this work is to isolate stress-induced electrical property changes from the electrical property changes resulting from changes in the nanowire's crystal structure. Another new user project is exploring the independently electrically addressable cantilever beams on the platform (see Image 3) in order to measure in situ strain in battery electrode materials during lithiation and delithiation. This work, led by Prof. G. Gulley of Dominican Univ., "Measurement of Stress Generation in Li-ion Battery Electrodes Using the CINT Discovery Platform," has shown the measurement of reversible strain generation in porous graphitic carbon electrodes in ethylene carbonate based Li electrolytes. Future work in this project will explore the initial stages of electrolyte reduction during anode charging by examining in situ strain signatures that result from the deposition of organic reduction products on the electrode surface.

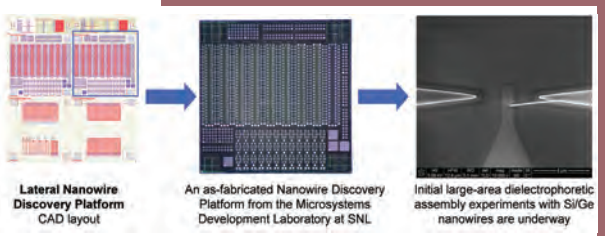


Figure 1. Lateral Nanowire Discovery Platform

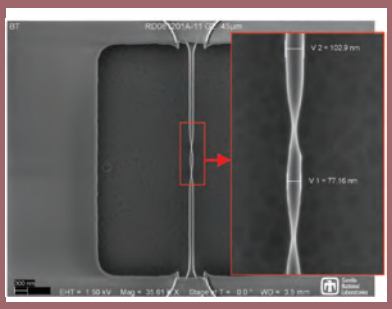


Figure 2. Silicon NWDP

Nanowire Discovery Platform (NWDP)

As a result of the significant level of CINT User and CINT research on semiconducting nanowires and CINT's Integration Focus Activity on Nanowires for Energy Applications, the Center has undertaken an effort to design and fabricate several versions of Discovery Platforms aimed at studies of 1-D nanowires, nanotubes and other novel materials, such as graphene.

Three different Nanowire Discovery Platforms (NWDP) have been designed for various experiments ranging from templated vertical growth of semiconductor nanostructures and the lateral device testing of such devices to the 'top-down' fabrication of silicon nanowire devices using an oxidation and etch-back technique compatible with semiconductor foundry processes. By using the substantial cleanroom facilities at Sandia National Laboratories, we can produce these Discovery Platforms in large numbers and with high yields. One of these Platform designs has passed completely through cleanroom processing and is in limited testing presently (see Figs. 1-2). The two other platforms are poised to emerge from device processing shortly.

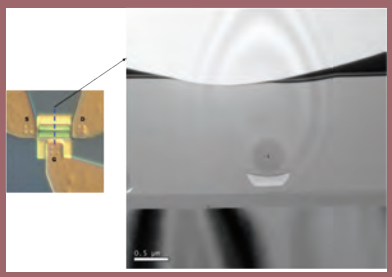


Figure 3. Cross-section of silicon nanowire channel on Si NWDP

Several initial experiments have been conducted by researchers at CINT and UCLA (Diana Huffaker) on the assembly and device integration of as-grown nanowires on the lateral platform (see Fig. 3). Further user interactions are expected once the vertical and Si nanowire platforms emerge from cleanroom processing.

Postdoc highlight - Shadi Dayeh

Shadi Dayeh, the post doctoral fellow at CINT who was recently promoted to the position of Oppenheimer fellow, has been lauded for his creative research on next generation electronic materials and devices, and for providing leadership to his peers. That success has emerged from his simple operating principle, "Every time a door opens, you widen your perspective on what you can do and how you can utilize your abilities, and that's what I've tried to do as best I could."

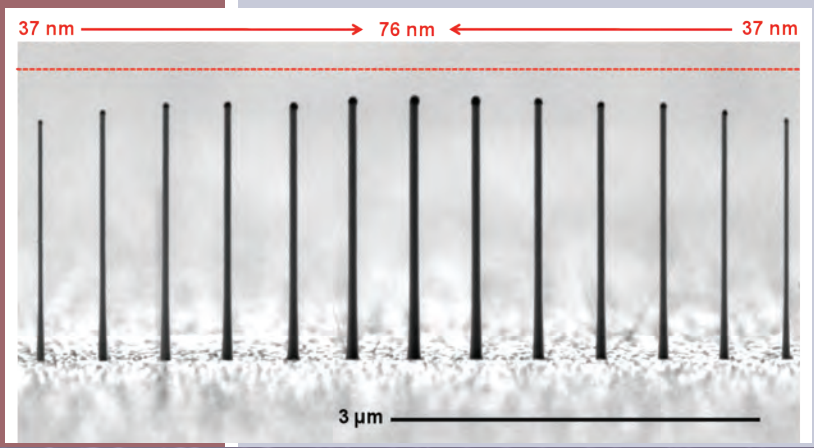
Evidently, Dayeh adopted this practice very early. At around age 5, growing up in a small village near Beirut, Lebanon, he began taking apart his toys and trying to modify each one to make a new toy. "I didn't always succeed," says Dayeh, "but I always had that curiosity to understand how things work." When his father brought him a truly exciting toy, a small, motorized jeep, Dayeh couldn't stop himself from prying it open, trying to understand the mechanics of how it worked, and then putting it back together to demonstrate to his friends its principle of operation. That was a first step toward falling in love with physics. For many summers that followed, Dayeh helped as a mechanic in an auto-repair shop owned by his family until the mid-1990s and once dreamed of being an electromechanical engineer for a Formula-1 car-racing team.

Electronics became Dayeh's central focus while a university student in Beirut, and then, in the Jacob's School of Engineering at UCSD, where higher impact problems became more evident to him. Dayeh did award-winning graduate work on indium-arsenide nanowires, ultra-thin whiskers of crystalline material with diameters from 10 to 100 nanometers (billionths of a meter). He not only cleared up a controversy on the growth mechanism of these wires, but demonstrated that electrons moved faster in these than in any other semiconductor nanowires, making indium arsenide wires a promising candidate for use in high-speed nanoelectronic devices.

In coming to Los Alamos as a post doc, he was leaving an engineering community and entering a basic science community, which, he reports, "opened up many pathways to seek advanced understanding of nanowire growth mechanisms and materials properties."

Dayeh has gone at these opportunities with his usual dedication, starting his workday at 10 am and never going home before 2 am the next morning, and often much later. "When I'm trying to solve a problem, I think about it all the time—driving, eating in a restaurant, even when I'm supposed to be sleeping. Especially when I'm growing nanowires, I feel like I go inside the sample, look at the wires, and feel a connection to the different processes that are going through them. I believe every scientist, when he goes into his deep thought, becomes one entity with the problem, and that's when he can reach a solution."

At CINT, the first project to engross Dayeh was a comprehensive study of the metal-catalyzed vapor-liquid-solid (VLS) method for growing very high quality nanowires. His detailed measurements and theoretical modeling demonstrated unequivocally how the basic laws of thermodynamics govern every aspect of the VLS growth process including the exact dependence of growth rate on wire diameter and the limit on how thin a wire can be grown by this method. Tom Picraux, Dayeh's mentor at CINT, comments, "This work is so beautiful that it can be used in textbooks to teach the principles of VLS growth."



SEM image of a bottom-up Germanium nanowires grown using chemical vapor deposition technique from e-beam lithography patterned Au discs with variable diameter.

Next, Dayeh took on the problem of using the VLS method to grow high-quality nanowire structures with a germanium core surrounded by a very thin shell of silicon, a problem that had stumped scientists since 2002. "The motivation for combining these two semiconductors in one structure," explains Dayeh, "is to develop next generation transistors that will have very high switching rates (teraherz compared to present rates of several gigaherz) and won't leak current when they're turned off."

There's no problem growing a germanium core wire using a tiny liquid-gold-seed catalyst. But when the temperature is turned up to deposit the silicon shell, the liquid gold that remains attached at one end, spreads along the germanium surface, destroying its desired current carrying properties. How could one prevent this problem without introducing extraneous contaminants? Dayeh came up with an elegant solution: grow in situ and at low temperature a very thin layer of silicon between the gold droplet and the end of the germanium wire, and thereby create a sufficient barrier to keep the gold in tact while the silicon shell is deposited.

It worked, and that opened the way to grow many different germanium-silicon nanowire structures. One, a germanium core surrounded by a p-doped germanium shell and finally a thin silicon outer shell, allows a strong current near the wire's surface and therefore a high sensitivity to external gating fields, suggesting that this combination of different materials is likely to be the basis for next generation high-speed transistors. A second structure, this time a 100%-germanium nanowire segment followed along the axis by a 100%- silicon segment, with nickel contacts at either end and a control gate attached near the silicon-nickel interface, has shown extraordinary current characteristics, namely, the "on" current is 10 million times stronger than the "off" current. Thus this axial structure allows much greater control over charge transport than current conventional transistor designs and Dayeh has hopes it will lead to new solutions to the leakage current problems in current integrated circuits.

Dayeh is a continual source of new ideas and is always sharing them with his colleagues, but the one he feels will have the most impact is a dense field of vertical nanowires, say a million on a square-millimeter substrate, that can be used as a probe to sense and stimulate neuronal processes in the brain. Dayeh and his colleagues will be pursuing this idea with funding from LANL's Laboratory Directed Research and Develeopment program.

Abundant talent and dedication notwithstanding, Dayeh credits his mentors with helping him get where he is today, and often expresses his desire to give back what he has received. Thus, Dayeh's ultimate goal is to become a professor at a leading research university because, as he explains, "there you have the greatest influence on society and on the new generations. There you can help people directly, and that is the most satisfying thing you can do."

User Conference

Users Executive Committee

The CINT Users Executive Committee (UEC) is an elected body of representatives that provides input from the user community to the CINT program management team, regarding facilities, operations, science, and quality of the on-site user environment. All UEC members are active CINT users, having either a current or very recently approved CINT user proposal. The current members are:

Prof. Dvora Perahia, Chair *Clemson University*
Prof. Richard Averitt *Boston University*
Prof. Suneel Kodambaka *University of California, LA*
Prof. Linda Peteanu *Carnegie Mellon University*
Prof. Elba Serrano *New Mexico State University*

In response to the growing community, in 2010, the UEC expanded the number of members to represent the demographics of the users adding representatives from the student/postdoc users, an industrial liaison, and is working with CINT to extend the scope of scientific expertise on the proposal review committee.

The UEC is heavily involved in planning the techical portions of the CINT User Conferences each year. During the conference, the UEC meets privately and also hosts an informal open forum for current and prospective users to share information about, and provide feedback on, CINT operations and management. This has resulted in lively, constructive dialogue targeted not only towards operational improvements but also to a better understanding of DOE, BES and CINT policies.

To foster open communication between CINT and the User Community, the UEC has quarterly conference calls with members of the CINT management team. These provide a forum for the UEC and management to formulate new initiatives, and develop a cooperative atmosphere in which to discuss and resolve user concerns.

In 2011, the UEC will co-organize the annual CINT User Confrerence, and UEC members will work with CINT staff on one or more focused workshops, including one targeted towards private-sector nanotechnology companies. CINT's UEC is also involved in the National User Facilities Organization event on April 7, 2011 to present the role of the national facilities to Congress.

CINT User conferences have been held every year since 2001 with increasing participation by users as well as the UEC. The Conferences have evolved into a dynamic forum that highlights state of the art research, carried out by CINT users and staff scientists, and external speakers in the fields of interest to the CINT community. The UEC participates in the planning and program content of the user meeting including selection of the invited speakers. The meeting format enables extensive technical discussion via open microphone periods following all lectures, together with a well-attended poster session featuring user science, CINT staff science, and facility information updates.

CINT held its 10th Annual Users Conference on August 9th-11th, 2010 at the Albuquerque Marriott Hotel in Albuquerque, New Mexico. There were 150 registered participants from 28 Universities, 3 Industries, and 5 Government Agencies and Laboratories.

Pedro Montano, the Director of the Scientific User Facilities Division, Basic Energy Sciences (BES) gave an update of goals and funding directions of BES, followed by three plenary speakers. Eva Andrei (Rutgers, The State University of New Jersey) demonstrated the existence of Dirac fermions in graphene, resulting in unusual transport properties; David Weitz (Harvard University) present routes to derive well defined colloidal particles for encapsulation using micro fluidics and Michael Thackery (Argonne National Laboratory) discussed Advances in material research for Electrochemical Energy Generation and Storage.

Continuing with our tradition of science symposia around active areas of user projects and research at CINT, three parallel symposia were held during the event. Carbon-based Nanomaterials Symposia, organized by Suneel Kodambaka (UCLA), Sasha Balatsky, and Steve Doorn, focused on recent advancement in formation and interactions of new carbon based materials. The Soft & Composite Nanomaterials Symposium organized by Dvora Perahia (Clemson

University and UEC Chair), Andy Shreve and Gary Grest, focused on optical response of single nano particles and assembly of nano-particles. The Nanomaterials for Energy Storage and Energy Conversion Symposia was organized by John Sullivan and Quanxi Jia. This collection of symposia featured presentations on the synthesis of nanoscale battery materials and complex, heteroepitaxial oxides, new characterization techniques using in situ TEM and AFM, modeling of battery materials and correlated electron systems, and controlling interfaces for energy storage and oxide nanocomposites. A Poster Session with contributions from Users and CINT scientists was held, as well as an optional tour of the Core facility with demos on our Discovery Platforms and 3D Viz capabilities.

The Conference was preceded by two highly attended events; a Nano-ed Materials Workshop run by CINT User and UEC member, Elba Serrano (New Mexico State University) and a focused Industrial Outreach Session. The goal of the one-day Nano-ed Materials workshop was to develop a repository of nano(bio)science educational materials that can be made available to educators in 2- and 4-year colleges. Workshop participants were encouraged to bring teaching materials to share with other educators that will be assembled and made available to the CINT Community.

CINT's Industrial Session titled "The Center for Integrated Nanotechnologies: A Business R&D Resource" attracted participants from over 50 small businesses in New Mexico. Speakers from the New Mexico Small Business Association, current industrial users, and CINT Management helped steer an interactive session defining how CINT can help small businesses and what resources are available for them to leverage the capabilities at CINT. Current user, Ed Flynn (President, Senior Scientific, LLC) was quoted as saying "Although we are a small company, the expertise and facilities at CINT have allowed us to perform more like a big company".

Save the date:

The 2011 CINT Users Conference will take place on Sept 14-15, 2011 in Albuquerque.

User Projects

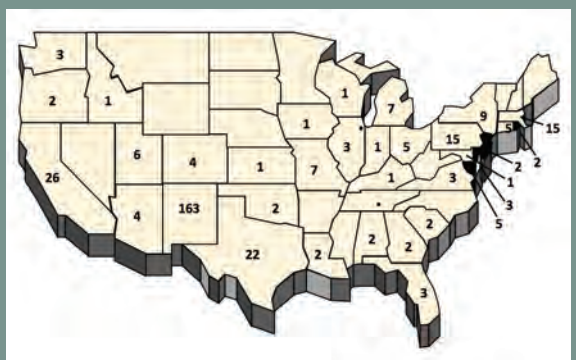
The CINT user program is designed to provide the international scientific community access to Core and Gateway Facilities. User access can include use of capabilities in either or both of our Facilities as well as engagement of the CINT Scientist staff expertise. There are two modes of user access: General User access and Partner User access, each with variable scope and the ability to conduct nonproprietary or proprietary research.

CINT users may conduct their approved research projects in collaboration with one or more CINT Scientists or may choose to access CINT capabilities independently. User proposals are evaluated on the merits of the science without preference for collaborative/independent access.

Users working independently will be properly trained and supervised by technical personnel. Some CINT capabilities cannot be operated independently for safety or complexity reasons.

User proposals consist of a 2-page (maximum) pdf document that is uploaded via the website along with user information entered on-line. All user proposals undergo an initial feasibility/safety screening by CINT technical staff, and a technical peer-review conducted by external Proposal Review Panels that reflect the four CINT Scientific Thrusts. The CINT Management uses the Review Panel scores and comments to prioritize access to CINT.

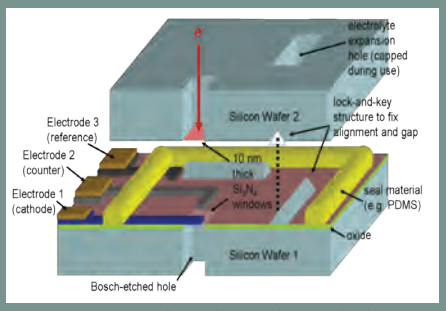
In 2010, CINT had 355 active projects, with users representing 34 states and 36 countries.



User Program

Industrial Focus

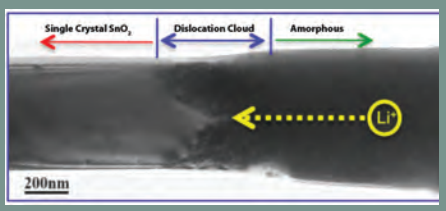
Interest in nanotechnology – and the underlying nanoscience— has grown explosively because of the perceived potential to beneficially impact almost every aspect of our lives. The remarkable scientific discoveries disappoint humankind if they cannot be exploited by technologies providing unprecedented functionality and performance. CINT capabilities and expertise can promote technology innovation via use-inspired research projects and teaming among industry, academia, and National Laboratory scientists.



In-situ TEM platform designed to study the atomistic changes of batteries during cycling.

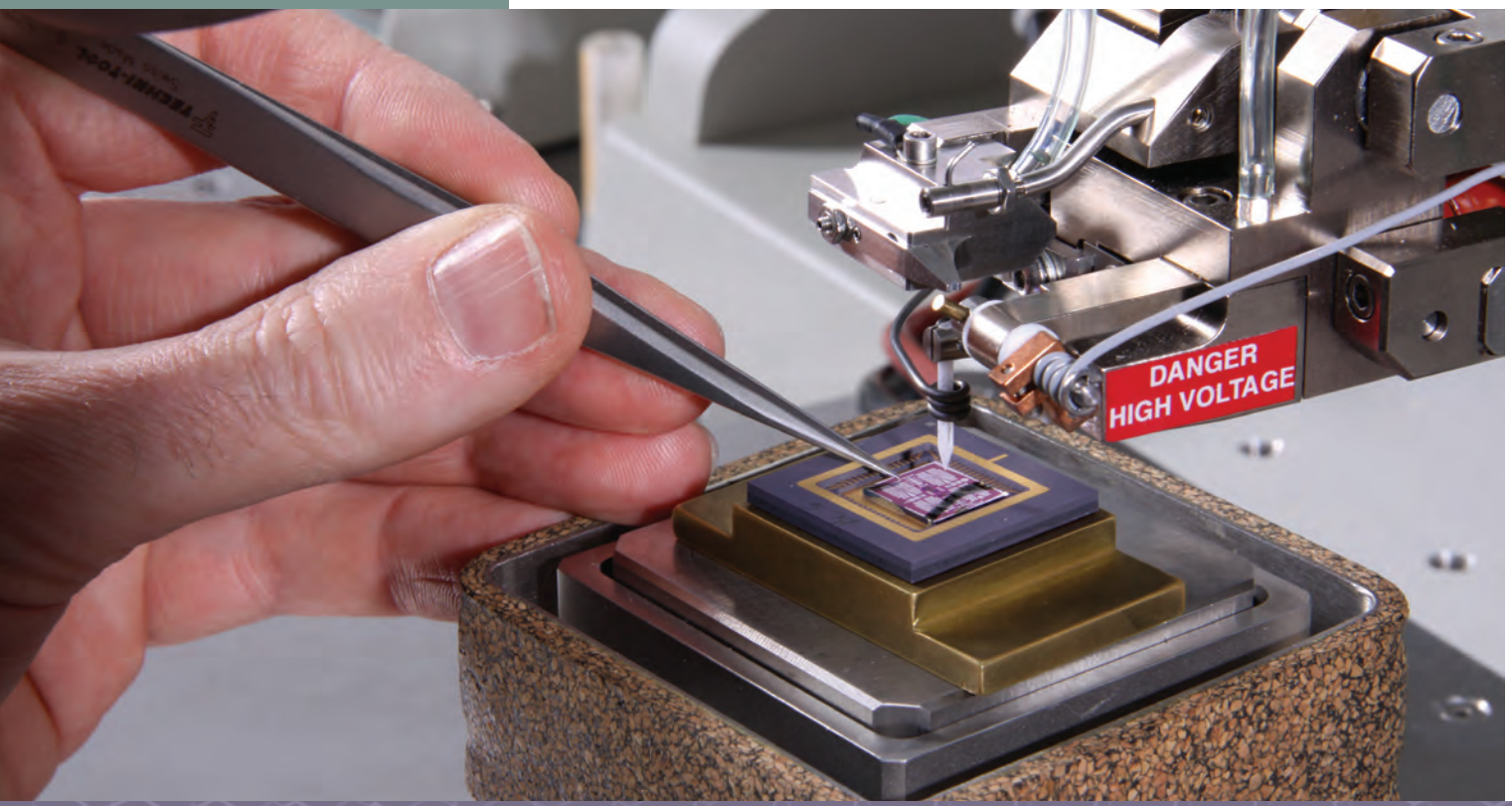
For example, numerous battery technologies have been proposed for the transportation and grid energy-storage sectors. However, all of the proposed battery technologies face similar challenges in meeting safety and reliability metrics needed to ensure public adoption. Currently, industry evaluates new technologies by performing large-scale testing of complete battery systems, after millions of dollars and multiple years of development effort. A predictive, science-based understanding of the atomic and molecular level materials chemistry processes could accelerate battery innovation.

CINT is pioneering new characterization methods directly relevant to battery research. The figures show a schematic of a new "discovery platform" (top) that will enable direct observation of nanoscale structural changes during battery operation. The in situ transmission electron micrograph of lithium insertion in a tin-oxide nanowire battery electrode (lower panel) illustrates the exquisite detail obtainable through such studies. These and other methods can provide the insights to develop improved electrode materials and understand degradation mechanisms.



TEM images lithium inserting into a SnO_2 nanowire.

CINT accepts hundreds of user-defined projects each year, generating knowledge that ranges from the most basic physics to valuable intellectual property protected by patents. Although the majority of the user projects involve pre-competitive research that will be published in the peer-reviewed technical literature, CINT users can also conduct proprietary research. We welcome the opportunity to stimulate technology through scientific understanding.



User highlight - Linda Peteanu

In her collaborations at the Center for Integrated Nanotechnologies, Linda Peteanu is hoping her work can help shed light on her science—literally. Peteanu, an associate professor of Chemistry at Carnegie Mellon University in Pennsylvania, has been coming to CINT every year since 2007 to conduct experiments on organic light-emitting diodes (OLEDs).

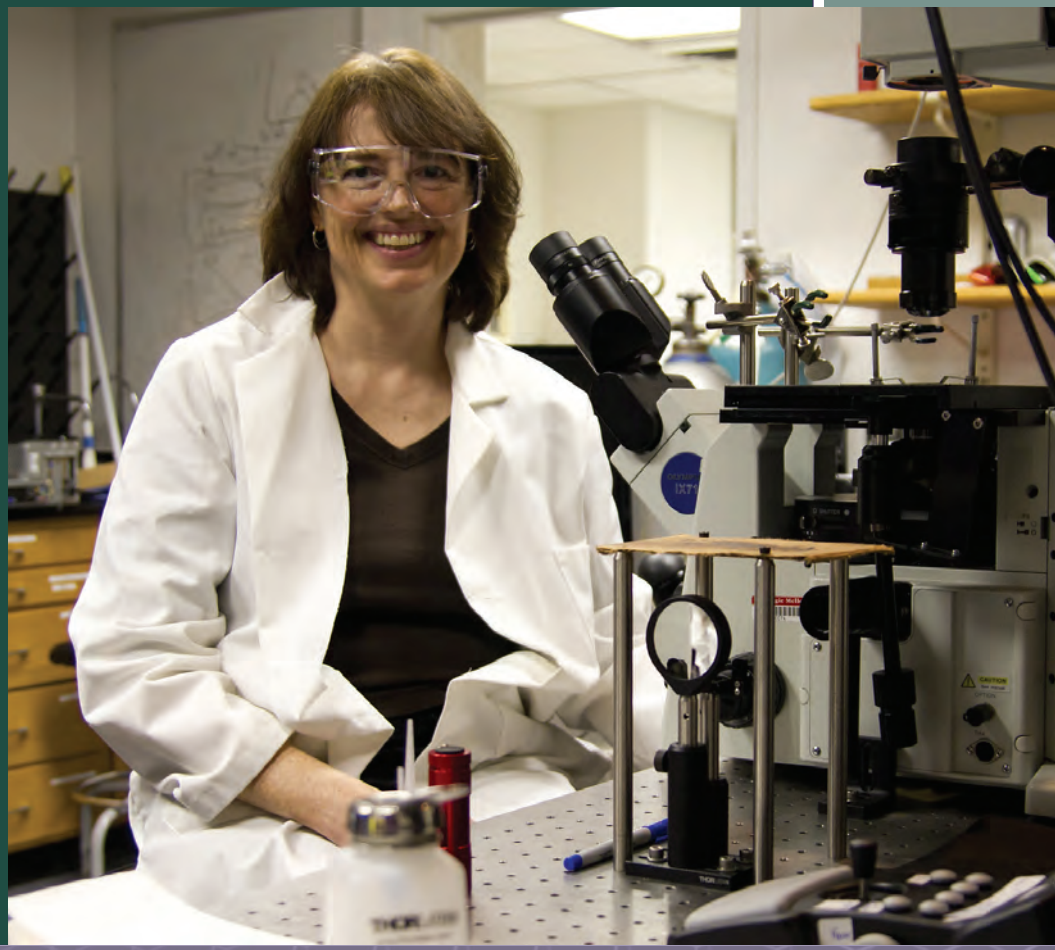
OLEDs are comprised of thin films of organic molecules that, when electricity is applied, generate light. Although still in their infancy, OLEDs promise a brighter light than conventional LEDs and more energy savings than incandescent bulbs.

Peteanu is studying the form, structure, and dynamics of the molecules used in OLEDs for organic lighting and for photovoltaic cells in solar panels.

Specialized CINT facilities have allowed Peteanu to delve deeper into understanding the molecules used for OLEDs.

In OLEDs, molecules isolated in solution are taken and applied as a thin film to make up the solid-state device. Peteanu has used CINT's time-correlated single-photon counting capabilities to try to understand how these molecules aggregate on the polymer film and how efficient their emissivity is, that is, how well they release photons in an excited state, creating light. "Put in solution, molecules behave one way. But we take them out and make them optically thick so you get more light out of them. We're interested in optimizing that emission to make organic lighting," she said. "We're essentially fundamental physical chemists, trying to figure out methods we can use to determine whether the materials used in these systems are aggregating, interacting strongly with one another, and changing their properties fundamentally."

In the last two years, Peteanu has finally been able to "see" what's happening. With images taken with CINT's fluorescent lifetime imaging microscopy, or FLIM, she can take the data from the time-correlated single-photon counting and combine it with images to discover what the polymer films or aggregated states actually look like. "You have a visual picture now and can see lifetimes of molecules and how they are forming structures in the solid state," she said. Her successful work has fit in well with the national user facility's goal of fostering scientific discovery. "Linda is a great user for this center because she came in with a well-defined problem and worked on it for an extended period of time," said Andy Shreve, CINT's thrust leader for soft biological and composite nanomaterials. "We're happy to make available the equipment to help her get her work done."



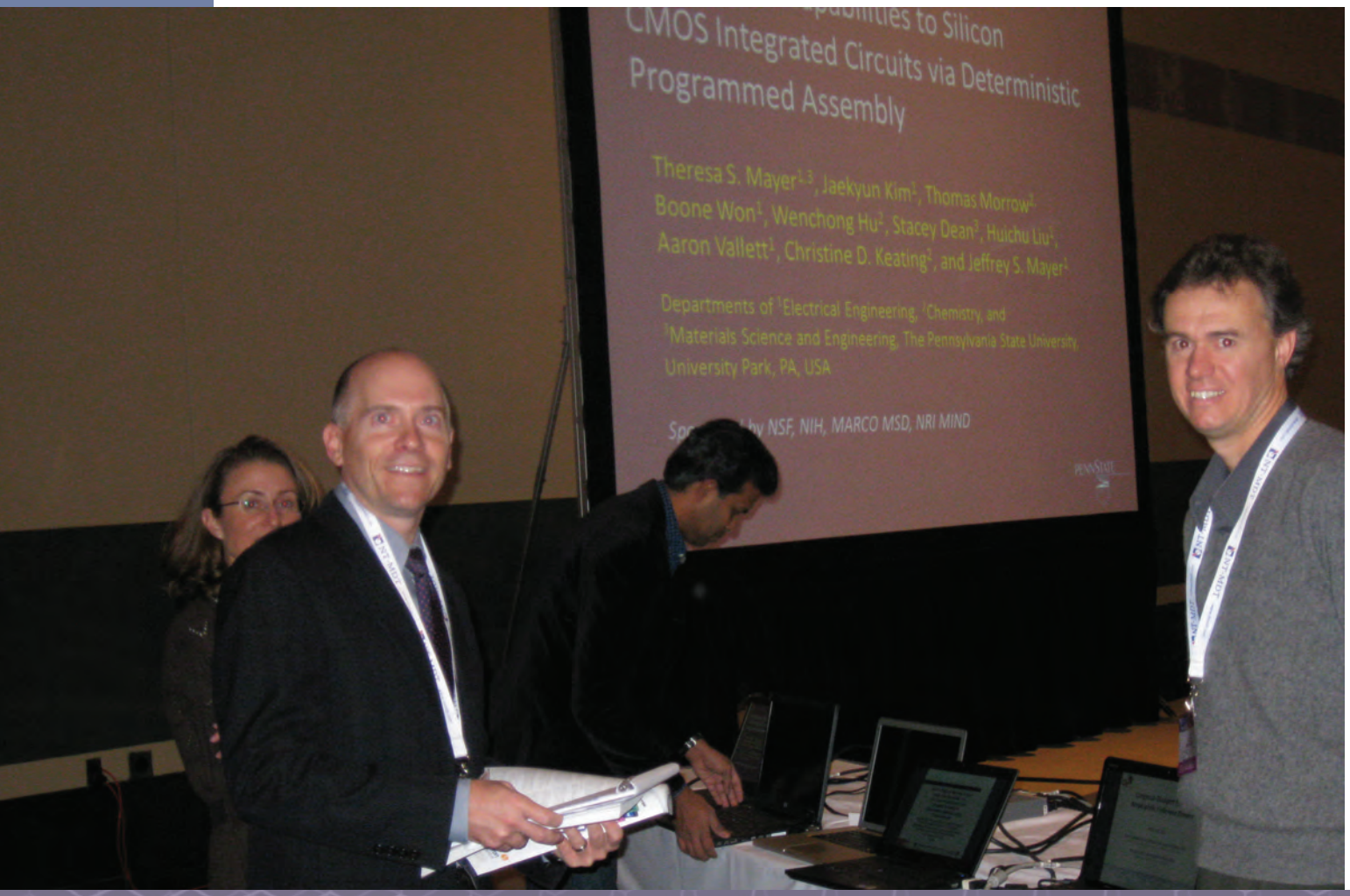
Peteanu has been able to extend her research at CINT to work on OLEDs in Pittsburgh. There, she is working with manufacturing companies to help them understand how the molecules and films in their existing OLED devices are behaving and why some systems are brighter than others. But perhaps just as rewarding is what she's gained from her interactions with CINT scientists in Los Alamos. "You're surrounded by experts who are there to help you. The instrumentation is wonderful, but the people aspect of it is also great. You have people to discuss the problems with you and think through the science, and people to read your manuscript and make comments," she said. "I consider these people my friends."

MRS Meeting

Symposium Y, Nanomaterials Integration for Electronics, Energy, and Sensing, was held at the Fall Annual Meeting of the Materials Research Society, November 29-December 3, 2010 in Boston, MA. The Symposium was organized by Tom Picraux (CINT chief scientist), Mark Reed (Yale University), James Hannon (IBM Research Yorktown Heights), and Wim C. Sinke (ECN Solar Energy, The Netherlands).

Summary of Symposium Y: Nanomaterials Integration for Electronics, Energy, and Sensing

A major theme of this year's Symposium Y was enabling improved performance in electronics, photovolatics, energy harvesting, and sensing by the incorporation of nanoscale materials. Specific areas described in the symposium included photovolatics, water splitting, nanoelectronics, and nanopower generation. One of the main drivers of nanotechnology is the realization that nanoscale materials can have superior properties that are often tunable. As the field matures, increasing emphasis is being placed on the challenges of integrating nanomaterials into devices in a scalable, cost-effective way. Advances in the areas of novel device architectures and scalable methods for synthesis and integration were particularly noteworthy. For example, H.A. Atwater (Caltech) and A. Polman (FOM, Amsterdam) showed that solar cells with periodic, nanopatterned interfaces can trap more light than cells with planar interfaces. Clever nanopatterning can also be used to create unusual metamaterials with engineered optical properties (e.g. with a negative index of refraction). Several authors noted that nanomaterials can offer improved performance with potentially lower overall cost, as nanofabrication methods become more widely available. For example, advances in the large-scale assembly of semiconductor nanomaterials were discussed in detail by A. Javey (UC Berkeley), T. Mayer (Penn State). J. Rogers (U. Illinois) presented efficient transfer methods to incorporate nanoscale devices onto flexible substrates for applications in electronics and photovoltaics. T. Barwicz (IBM) described an oxidation process that can be used to produce "top down" silicon nanowires suitable for high-performance logic applications.



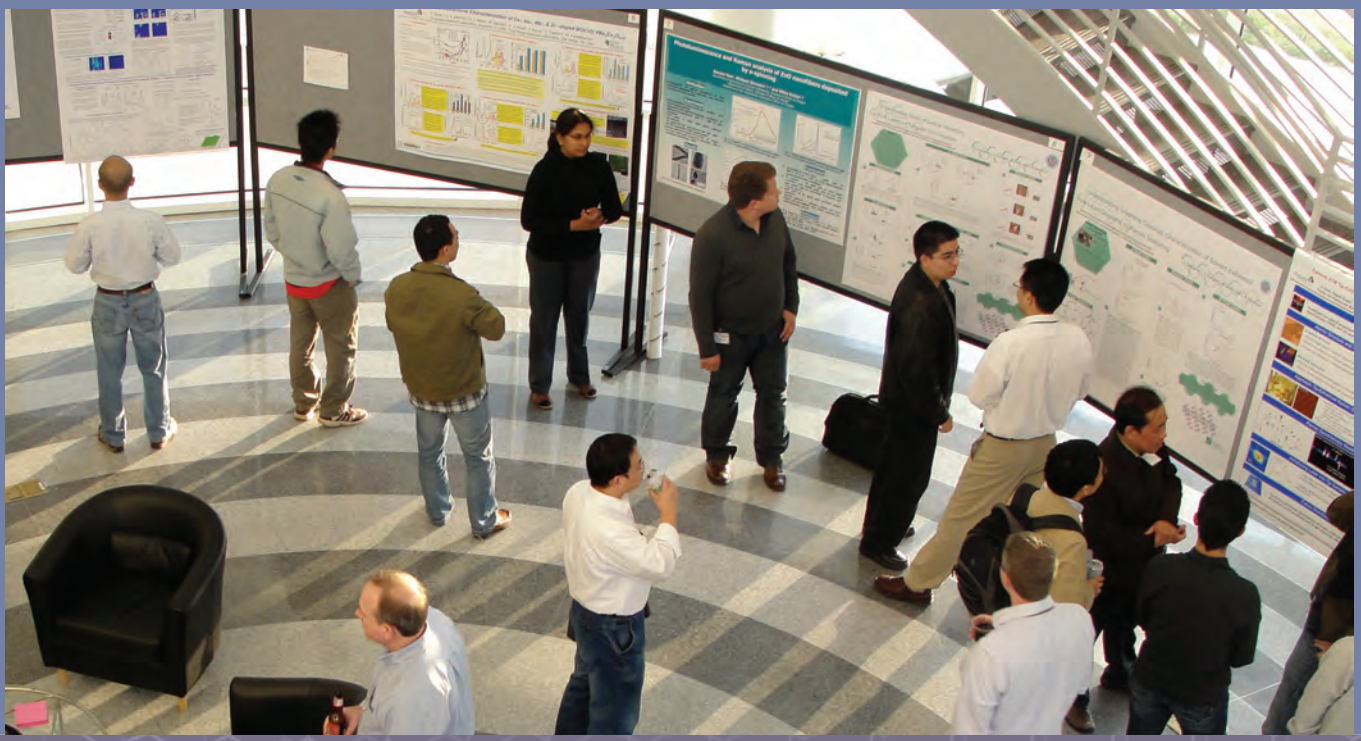
NSRC Workshops

The five Department of Energy Nanoscale Science Research Centers (NSRCs) have started holding joint workshops to expose the various levels of research and user projects that are ongoing at the five centers. These exchanges of information have provided the staff at the NSRCs with the opportunity to learn about topics/thrusts in nanoscience the other centers and to develop an understanding of the different areas of expertise among the staff members. They have also facilitated discussions towards possible future areas of collaboration between the centers and provided basic information so that potential NSRC users can be directed toward the optimal center and staff to meet their research needs.

Two workshops were held in 2010. CINT hosted the Theory and Simulation of Nano Scale Materials workshop, and the Center for Nanoscale Materials at Argonne National Laboratoty hosted the Applications of Raman Microscopy to Nanoscience Workshop. Future workshops on special topic areas, such as reactions at surfaces and interfaces, soft-matter and self-assembly, and energy storage and conversion materials, will be set up to further facilitate collaboration between the centers. These workshops are open to NSRC users and those interested in working with the NSRCs. To inquire about these and other workshops in which CINT is involved, please see the CINT website or contact Neal Shinn.

Theory and Simulation of Nano Scale Materials:
The Theory and Simulation of Nano Scale Materials workshop was held at CINT on October 14-15, 2010, to discuss recent developments in the theory and simulations of nanomaterials. The meeting consisted of 26 invited presentations, all but two of which were given by staff at the five NRSCs. Topics of interest included: Structure, Electronic and Optical Properties of Nanomaterials Electron, Proton and Energy Transport Catalytic Processes on the Nanoscale Soft and Bio Materials for Energy Applications Interactions at Nanoscale Interfaces Electronic, Optical and Magnetic Materials Nano Scale Self-Assembly and Emergent Phenomena Algorithm Development

Applications of Raman Microscopy to Nanoscience:
A workshop on Applications of Raman Microcopy to Nanoscience was hosted by the Center for Nanoscale Materials at Argonne National Laboratory on October 22-23, 2010, featuring the recent scientific research of NSRC scientists and users with respect to their Raman microscopy and spectroscopy capabilities. The workshop consisted of a full day of talks, an evening poster session (pictured below), and a short course program ofering hands-on demonstrations of the CNM's Raman microscope, an overview of Raman spectroscopy, and a tour of the CNM facilities. The oral presentations on Friday consisted of two plenary talks that covered both historical perspectives and recent results concerning surface-enhanced-Raman spectroscopy and graphene.



Patents

CINT Scientists were involved in nine patent applications in 2010.

Mid-Infrared Tunable Metamaterials - Igal Brener (issued)

3-Dimensional Imaging at Nanometer Resolution - Jim Werner, Peter Goodwin, Andy Shreve (issued)

Buffer Layer for Thin Film Structures - Quanxi Jia (issued)

Polymer-Assisted Deposition of Films - Quanxi Jia (issued)

Near Single Crystalline, High-Carrier Mobility Silicon Thin Film on a Polycrystalline/Amorphous Substrate - Quanxi Jia (issued)

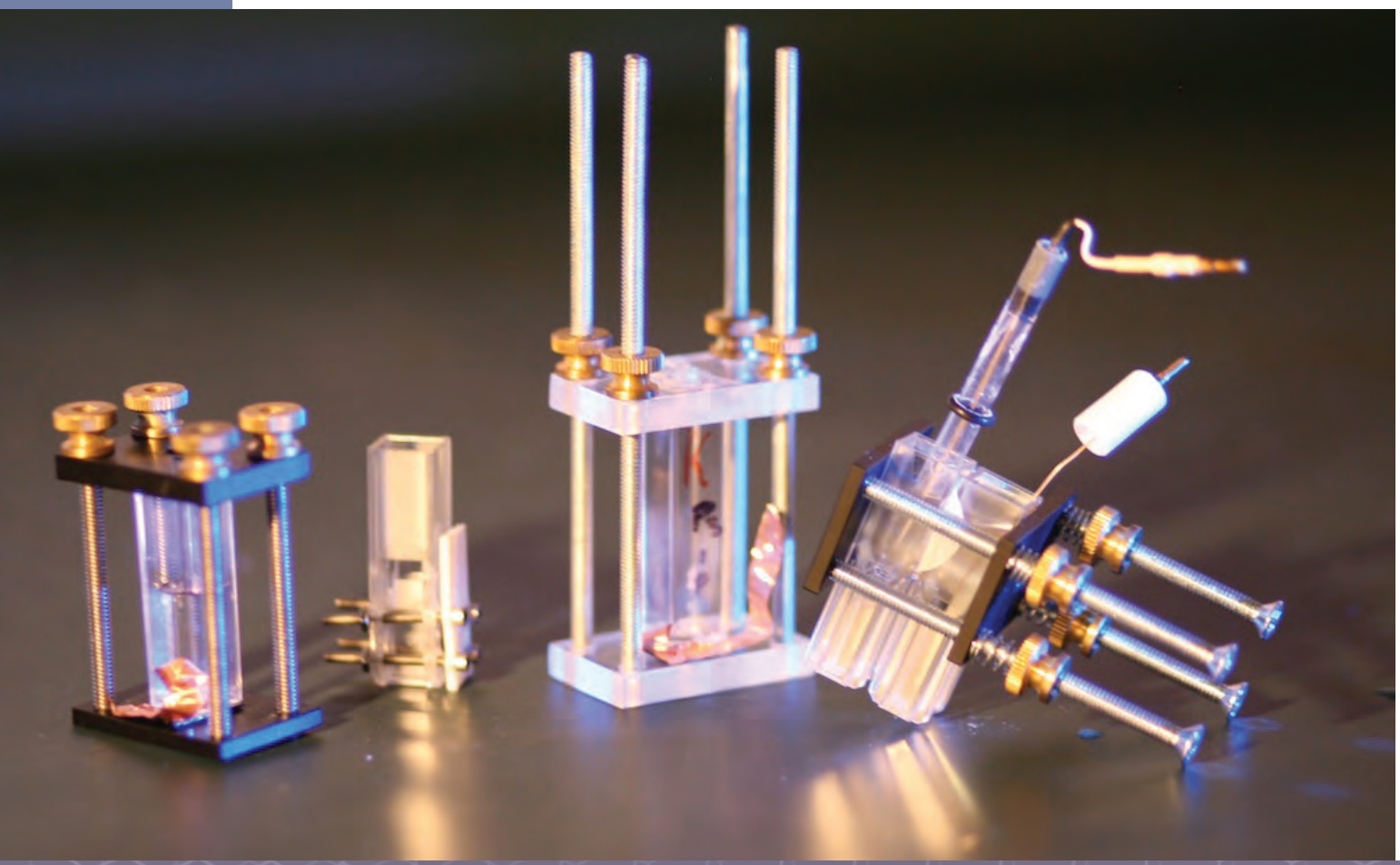
Apparatus and Method for Tracking a Molecule or Particle in Three Dimensions - Jim Werner, Peter Goodwin (issued)

Method for Transferring Strained Semiconductor Structure - Mike Nastasi (issued)

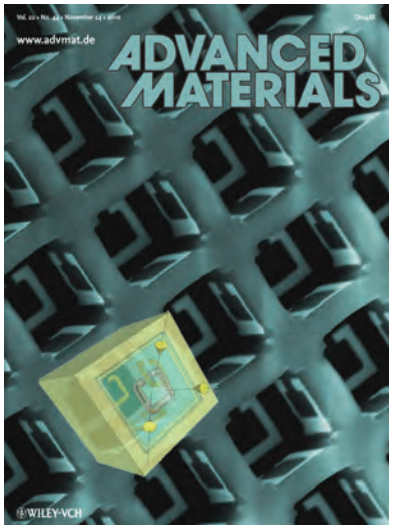
Fluorescent Metal Nanoclusters - Jen Martinez, Jim Werner (disclosed)

Electrochemical Apparatus Comprising Modified Disposable Rectangular Cuvette - Andrew Dattelbaum (disclosed)

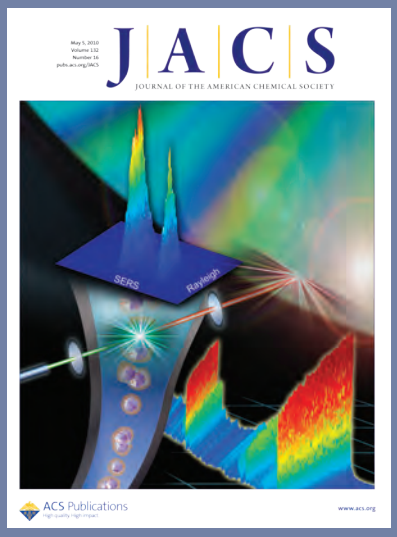
To help achieve our CINT scientific goals, we designed an electrochemical cell that consists of an inexpensive clamp and a disposable cuvette (below). This design allows one to run multiple electrochemical experiments simultaneously and minimizes issues of contamination between experiments as the reaction chamber is disposable. The electrochemical cell is suitable for a variety of electrochemical experiments, including surface electrochemistry, bulk electrolysis, and flow cell experiments, which further distinguishes our design from the electrochemical cells currently available today. These disposable electrochemical cells will be useful for a variety of basic and applied science areas such as characterizing organic and inorganic thin films for sensing, biofouling or corrosion applications, as well as for studying gas diffusion electrodes for fuel cell applications.



Cover Images

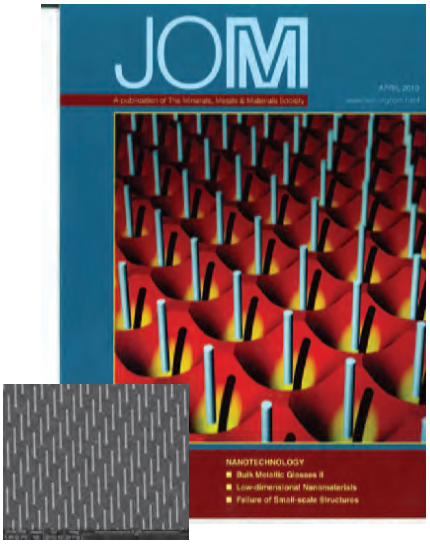


Membrane projection lithography is used to deposit split ring resonator structures (SRRs) on the interior faces of a cubic SU-8 cavity in work reported by Bruce Burckel and co-workers on p. 5053. The arrows in the inset schematic diagram show three of the five evaporation directions, while the SEM image shows the resulting metamaterial layers with SRRs on each of the five interior faces of the 6-μm cubic unit cell.
CINT Contact: Igal Brener

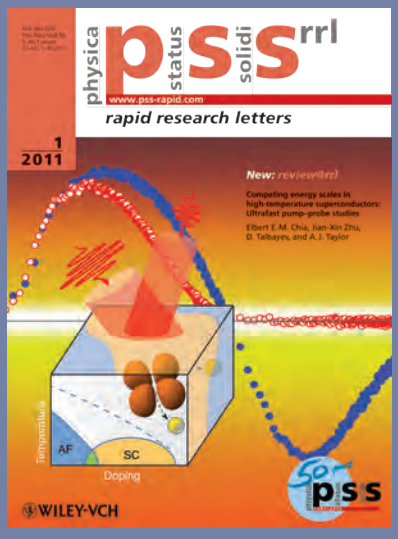


Full spectral high-resolution Raman detection for high-throughput flow-based nanoparticle analysis allows rapid characterization of large populations of surface-enhanced Raman (SERS)-active spectral tags. Evaluation of spectral variability at the single-nanoparticle level via simultaneous multiparameter optical measurements reveals subpopulations in SERS response that are correlated to individual nanoparticle geometries.
CINT Contact: Steve Doorn

Assembly of plan-view SEM images of GaAs pyramidal structures grown on nanopatterned substrates by MOCVD. Three types of equilibrium crystal shapes with distinct crystal facets are formed in patterns of different diameters (columns) and in different regions of the patterned samples (rows).
CINT Users: Ping-Show Wong & Dianna Huffaker (UCLA), CINT Contact: Aaron Gin



An array of orderly, vertical nanowires are shown in this illustration by Steve Neal of the University of California at Berkeley. Artists rendition of inset scanning electron image of vertically aligned nanowires grown at CINT.
CINT Contact: Tom Picraux



The figure depicts the phase diagram of high-temperature superconductors, where the antiferromagnetic phase, pseudogap phase, and the superconducting phase emerge, and sometimes even coexist or compete with one another, at different hole dopings.
CINT Contact: Toni Taylor

Spherical gold nanoparticles (not shown) are asymmetrically coated with S-(CH2)17-COOH ligands in water. S atoms are shown in yellow, CH2 chains in blue, COOH groups in red.
CINT Contact: Gary Grest

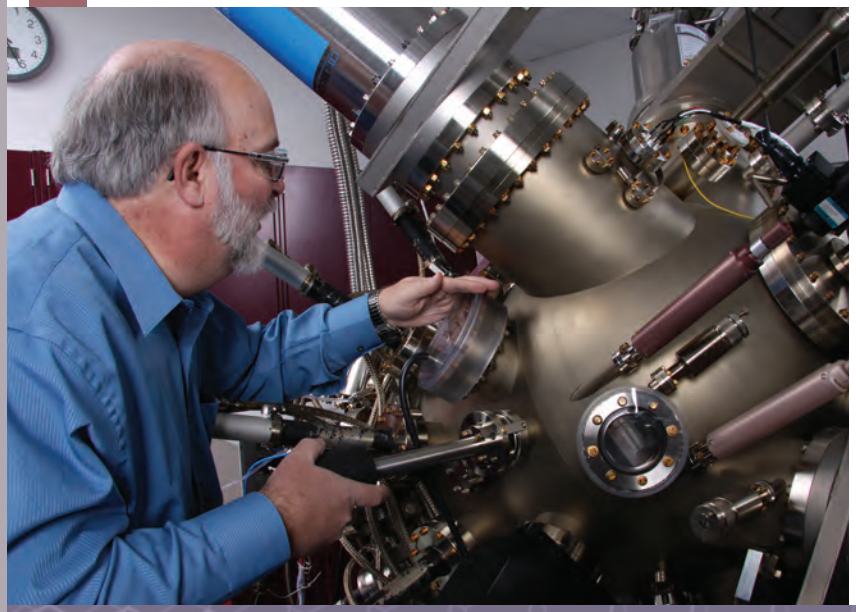
Nanoscale Electronics & Mechanics

This thrust is focused on understanding and controlling electrical and mechanical properties arising from confinement on the nanoscale, interactions within nanostructures and the integration of heterogeneous nanostructures for higher levels of functionality. Reduced dimensions and the influence of surfaces and interfaces give rise to unique properties not found in micro- and macro-scale systems. For electronic and mechanical systems, important integration issues involve energy transfer across interfaces, the role of defects in nanostructured materials, and interactions between nanoscale building blocks in integrated structures. These scientific issues arise in both electrical and mechanical nanosystems as we bring nanostructures together to implement specific functions, combine different materials to modify electrical or mechanical behavior, or texture materials on the nanoscale.

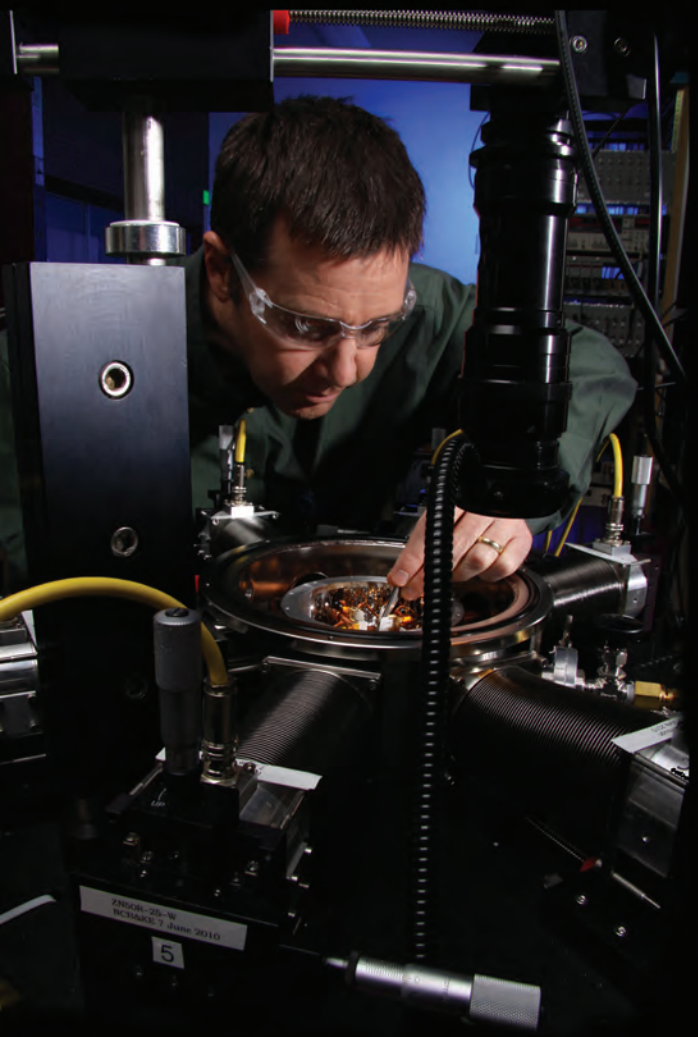
Research activities in the past year, many as part of active user projects, have focused on electronic, thermal and structural properties of nanowires and nanowire heterostructures, elastic and fracture properties of nanoporous and heterogeneous nanoscale materials, high-mobility 2D GaAs based materials and interactions of low dimensional systems, quantum computing in silicon or GaAs based semiconductors, nanomanipulation and integration of nanowires, and investigation of materials interface properties and functionalities.

Notable accomplishments in nanowire research include establishing the thermodynamic basis for the size dependent growth rate for germanium nanowires, and developing a process to spot-weld nanowires into electrical contacts on measurement platforms enabling reliable measurements of nanowire properties. Research on nanomaterials for energy storage applications was highlighted by creation of the world's smallest battery inside a transmission electron microscope, enabling real time observations of electrochemistry process at atomistic length scales for the first time. In structural studies of nanoporous materials we determined that structures with well-aligned long nanoligaments exhibit over 50% higher hardness and stiffness than the structure with short random-oriented nanoligaments. Studies of transport properties in nanoscale materials was highlighted by novel optical detection of electron-hole transresistance in a single layer of GaAs and measurement of the transport characteristics of silicon MOSFET-based gated double quantum dots. We determined that even in the presence of disorder in the MOSFET structures, the coupling between the dots can be smoothly varied. Our Discovery Platform work featured a new capability to perform combined electrical and mechanical measurements on individual nanowires.

In the coming year our nanowire research will target Si/Ge heterostructure device performance not possible with bulk materials based on CINT advances in high quality Si/Ge axial and core/shell heterostructure growth, and will take advantage of new capabilities including our thermoelectric measurement platform. Exploration of nanoscale materials for energy storage will include demonstration of novel high-capacity Li ion batteries based on Si nanowire anode configurations and continuing use of our in-situ nanobattery platforms, including a fully encapsulated liquid TEM cell, to search for materials that have high energy density, power density, and improved cycle lifetimes. Studies of transport properties will target single-electron occupation of Si MOSFET quantum dots and optimizing growth conditions and structures to provide high mobility 2-D hole gas structures. Research on structural and mechanical properties of nanostructured materials will focus on in-situ deformation studies of the effect of annealing on response in nanofoams and the effects of lattice strain on the properties of epitaxial perovskite oxide films.



Double Quantum Dots in Silicon MOSFET Nanostructures



Scientific Accomplishment:

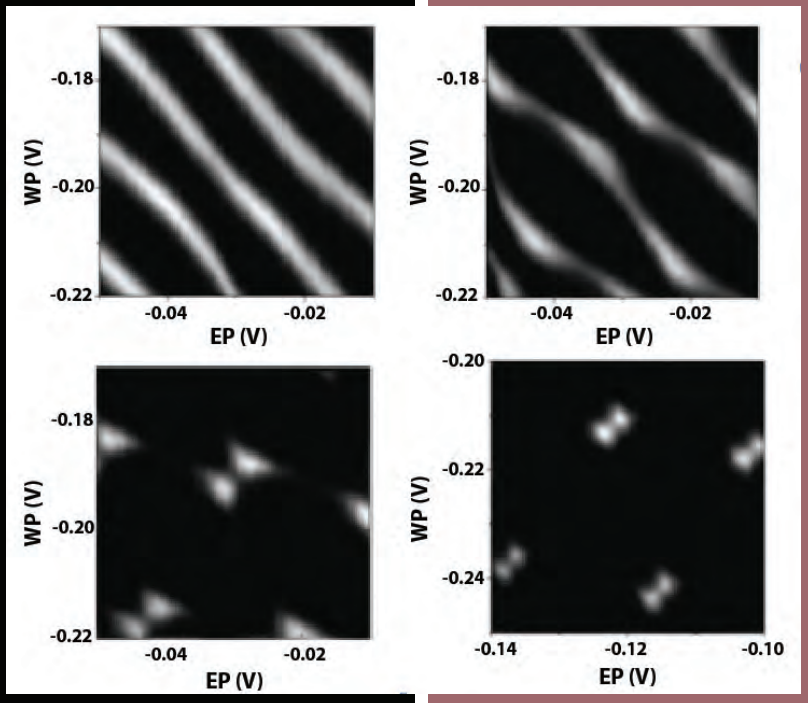
Electron spins in semiconductors is an attractive approach for quantum computation due to our ability to electrically tune the coupling between spins and to measure single spins using a spin to charge transduction. Quantum bits, or qubits, can be encoded in either the spin up/down property of a single electron spin, or in the singlet/triplet total spin of a two electron double quantum dot. In our work, we have made double quantum dot structures in silicon MOSFET devices. One advantage of silicon in spin quantum computation is the zero nuclear spin of the primary isotope, 28Si. Very long coherence times (>1 sec) have been demonstrated in spin ensembles in isotope enriched silicon material. While both GaAs and SiGe devices benefit from an epitaxial interface where the electron spins are confined, MOSFET structures must contend with an amorphous SiO2 interface. When faced with this more disordered interface, can the electrical control of the coupling between quantum dots be demonstrated?

Our MOSFET devices have two gate layers with the lower layer patterned into depletion gates and the upper layer serving as an overall accumulation gate. The upper gate is fixed at a positive voltage that accumulates electrons in a 2D system, and then the depletion gates are biased negatively to locally deplete electrons and form two quantum dots. The coupling between quantum dots is controlled with a single gate between the two dots. Transport is measured through the double dot system while the number of electrons on the dots is varied with two plunger gates (labeled EP and WP in the image below). Current flows only when the energy levels of the double dot system lines up with the Fermi energy in the source and drain region.

Significance:

Our transport studies show a smooth transition from strong to weak coupling in a silicon MOSFET double quantum dot. Thus even in the presence of disorder in the Si/SiO2 interface, coupling can be smoothly controlled. These results are important for the control of single electron spin coupling for future potential quantum computing applications.

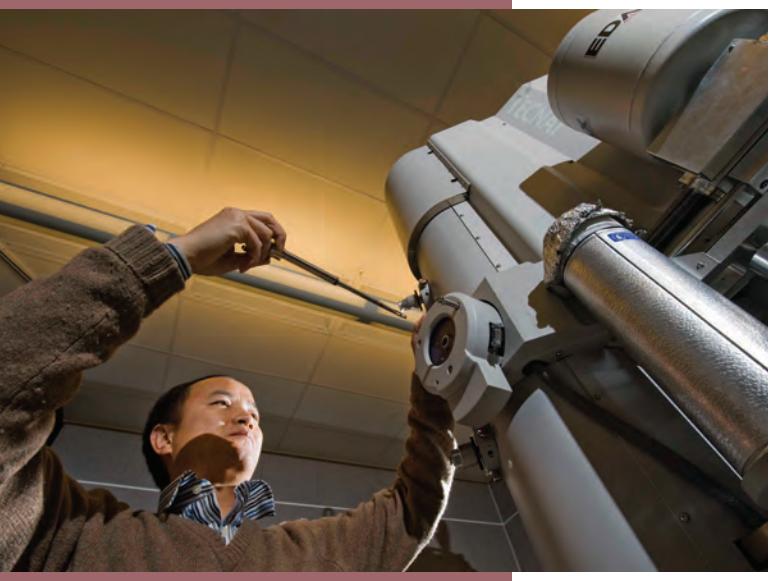
High (~pA) currents are shown as bright regions in the figure below. When tunnel coupling is strong, the double dot behaves as a single large dot and diagonal lines are observed. As the coupling decreases the transport makes a transition to triple points typical of double dot systems (lower right).



CINT contact: *Mike Lilly*

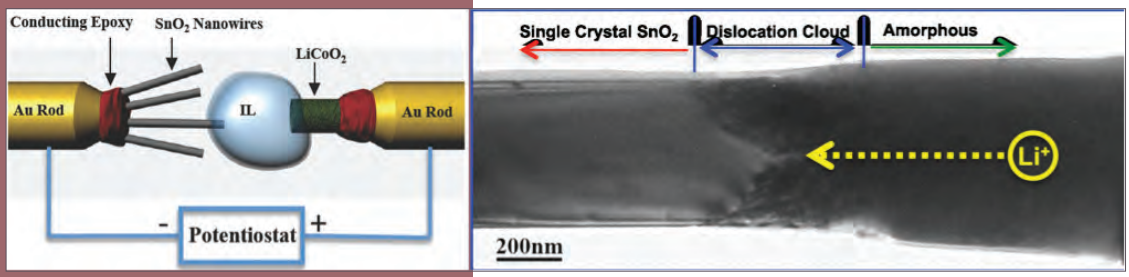
L. A. Tracy, et al., Appl. Phys. Lett. 97, 3518058 (2010).

The In situ Nanoscale Probe of ElectroChemistry by TEM



Scientific Accomplishment:

We have developed a new tool for studying electrochemical processes in real-time with nanoscale to atomic-scale spatial resolution. This tool is comprised of a special platform consisting of three parts: 1) a counter-electrode, 2) an ionic liquid electrolyte, and 3) a nanoscale working electrode mounted on a piezo nanomanipulator which altogether are housed within a high resolution transmission electron microscope (TEM). This In situ Nanoscale Probe of Electrochemistry by TEM, which we call INSPECT, allows – for the first time – the real-time measurement of liquid electrochemical processes with atomic to nanoscale spatial resolution inside a TEM. Recently, we have used this tool to investigate the mechanisms of electrochemical lithiation of a nanowire anode material, providing new insight into the fundamental processes that occur during charging of real Li-ion batteries (Science 330, 1515 (2010)). Using this tool, we can provide unprecedented spatial and dynamic resolution for the study of a wide variety of important electrochemical processes, such as those that occur in advanced batteries, electrodeposition, corrosion, and electrochemical etching. We expect that this tool will become an important capability for research efforts that are aimed at developing new materials and processes that would lead to ultra-high capacity and ultra-high rate capability batteries and super-capacitors to enable a new generation of long-range electric vehicles or large-scale electric storage systems for the power grid.



A nanobattery setup inside a TEM. (a) The nanobattery is consist of a single nanowire anode, an ionic liquid electrolyte, and a LiCoO2 cathode. (b) The single tin oxide nanowire anode was charged up. The reaction front contains high density of dislocations, meaning that the nanowire sustains a pressure of higher that 10 GPa without breaking, proving that nanowires are very good battery electrodes.

Our tool is based on a very important innovation involving the use of lithium salt-containing ionic liquid (IL) electrolytes inside a TEM. These electrolytes have the remarkable property of remaining in the liquid state with negligible vapor pressure inside the high vacuum of the TEM. We have first applied this tool to the problem of Li-ion batteries, which is the most important battery technology driving the next generation of electric vehicles. Within this field, there is intense interest in developing higher capacity batteries through the use of new types of high capacity anodes. Using INSPECT, we have tested one of these new anode materials, SnO2 nanowires, and discovered new and unexpected strain accommodation mechanisms during electrochemical lithiation (see the movie at: http://mt.seas.upenn.edu/Stuff/JianyuHuang/Upload/S1.mov). Importantly, we note that these mechanisms could not have been discovered using conventional electrochemical characterization techniques (such as cyclic voltametry) nor by other in situ characterization tools, such as in situ x-ray diffraction or in situ Raman (which do not have high spatial resolution).

Significance:

The current battery market is over $50 billion annually with demand expected to double within the next five years. The US DOE's projections for the Li-ion battery market for electric vehicles could be up to $24 billion by 2015. Clearly, our future transportation industry and economic competiveness will be closely-tied to innovations regarding new battery development. We expect that INSPECT will be an important tool to enable this new revolution in electrical energy storage.

CINT Contact: *Jianyu Huang*
User Proposal: U2010A901
Publication: JianYu Huang, Li Zhong, Chong Min Wang, John P. Sullivan, et al. In situ observation of the electrochemical lithiation of a single SnO2 nanowire electrode, Science 330, 1515-1520 (2010)

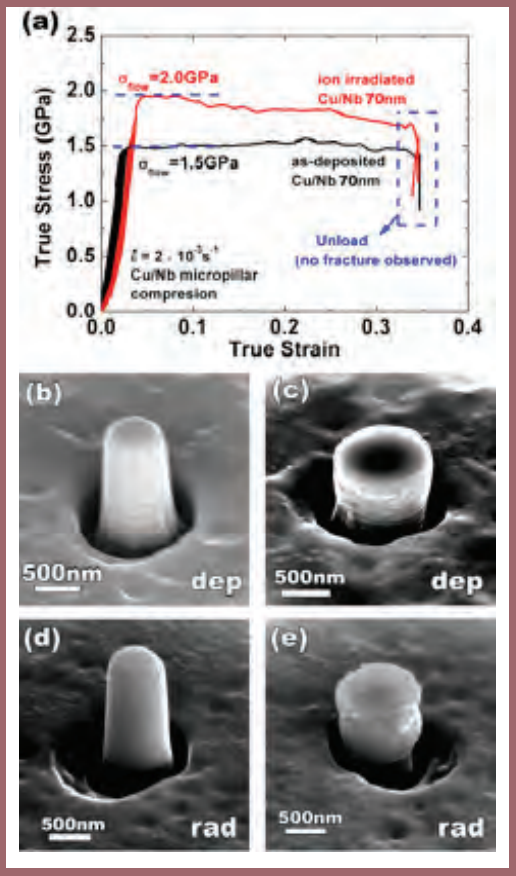
Compressive Behavior of He Ion Implanted Nanoscale Cu/Nb Multilayers

Scientific Accomplishment:

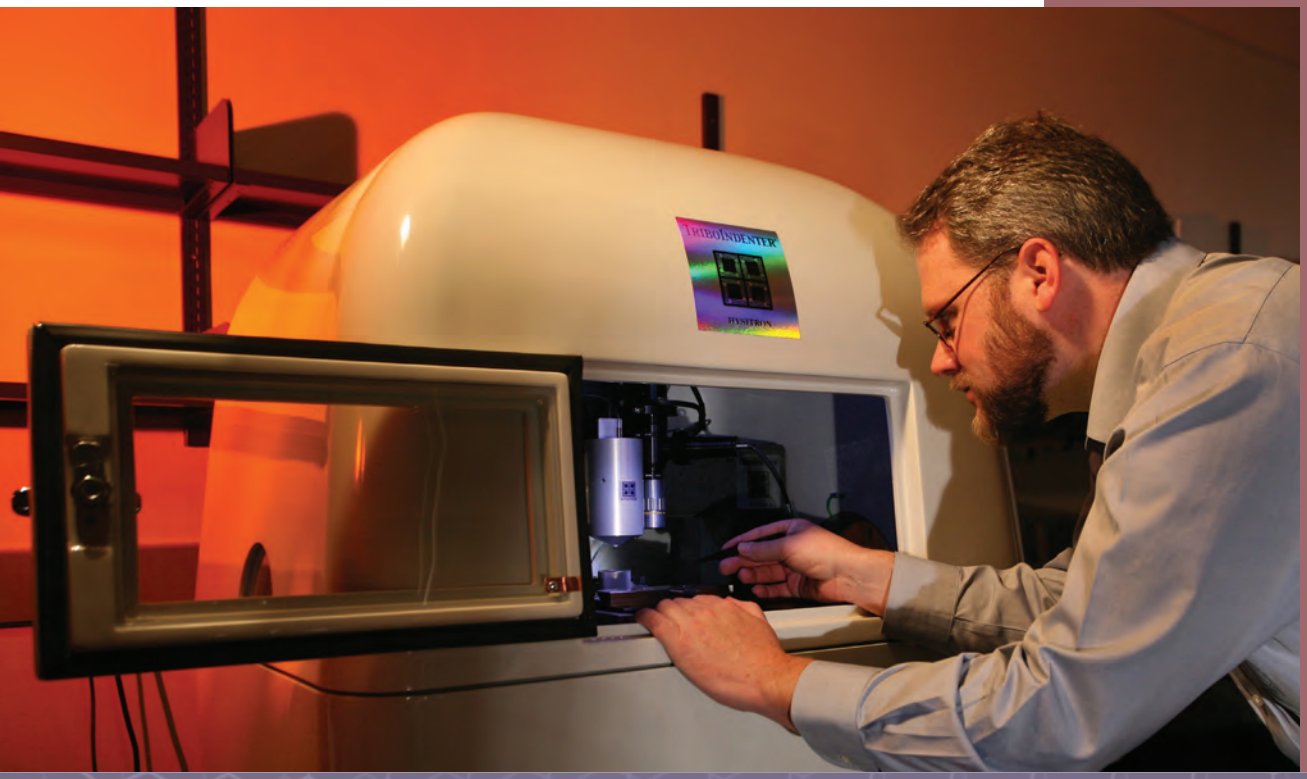
In order to extend the reliability and lifetime of structural materials for application in advanced nuclear reactors, a fundamental understanding of the mechanisms behind radiation-induced micro-structural damage is of paramount importance. The implantation of helium (He) ions in metals is a topic of recent investigation, due to He generation by endothermic (n, α) reactions during high-energy neutron irradiation in fusion reactor environments. In most engineering materials, radiation damage is marked by hardening (strengthening) accompanied by a reduction in ductility (brittleness). We have recently found that nanolamellar metallic composites exhibit enhanced radiation damage tolerance due to the high density of interfacial content containing sites that are favorable for irradiation-induced defect recombination. This work demonstrates in the Cu-Nb system at 40 nm layer thickness and below, implantation hardening occurs with no significant change in compressive deformability (strain ~30% without fracture).

Significance:

As an insoluble species, He preferentially combines with vacancies to form bubbles, resulting in swelling, blistering of metal surfaces, and embrittlement, which eventually deteriorate the structural integrity of materials and lead to reduced service time in nuclear reactors. In this case, the ability to synthesize high-strength nanolaminar composites with excellent radiation damage tolerance can lead to integration of materials with a high density of designed interfaces into next-generation nuclear reactors.



Mechanical behavior of 40nm CuNb nanolayered composite in as-deposited and irradiated conditions. (a) The stress-strain response of material in both conditions. Note the enhanced strength of the red irradiated curve, with no sacrifice of deformability. Most engineering materials would show a marked decrease in ductility after irradiation to 6-8% He content. (b+c) SEM micrographs of as-deposited micropillar before and after deformation, respectively. (d+e) SEM micrographs of irradiated micropillar before and after deformation, respectively. Note the similarity between deformation behavior in the as-deposited and irradiated state.



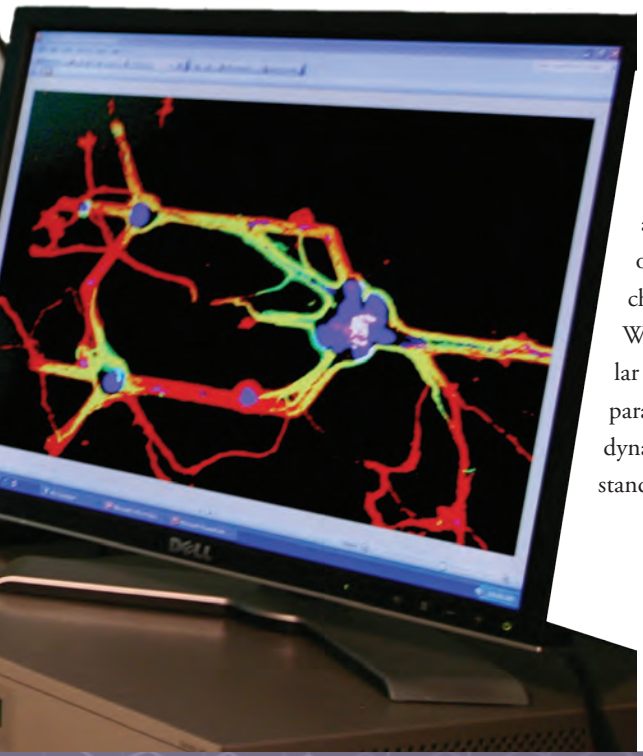
CINT Contact: *Nathan Mara*
User Proposal: C2010A971
Publication: Nan Li, N.A. Mara, Y.Q.Wang, M. Nastasi, A. Misra, "Compressive behavior of He ion implanted Nanoscale Cu/Nb Multilayers", Scripta Materiala (2011) in press.

Soft, Biological & Composite Nanomaterials

The Soft, Biological and Composite Nanomaterials Thrust focuses on solution-based nanomaterials, and targets improved understanding of how to integrate disparate classes of materials to produce functional results. Inspiration is drawn from a long-term grand challenge in nanoscale materials research, which is to be able to mimic the exquisite structures and functions that Nature produces through the synthesis, assembly, reconfiguration and exploitation of disparate components. Activities of the Thrust are directed toward key scientific areas: 1) Controlling interfaces and interactions between disparate classes of materials across multiple length scales; 2) Developing and applying new characterization tools for studying soft, biological and composite systems on multiple length and time scales; and 3) Exploring the roles of disorder and dynamics in controlling the performance of functional soft, biological and composite materials. Within this framework, topics include synthesis of multi-component nanoscale building blocks, assembly of components using both active and passive assembly methods, development of instrumentation for characterization of complex, disordered and dynamic composite materials, the study of dynamic and reconfigurable surfaces and interfaces, the incorporation of soft or biological materials into micro-scale device architectures, and the development of membrane-based composite materials.

Recent efforts, many of them in collaboration with CINT users, have explored all three of our scientific theme areas. Highlights in the area of controlling interfaces and interactions between disparate classes of materials include the use of lithographic processing and chemical patterning techniques to establish dual guidance cues, both physical and chemical, on material surfaces. These methods enabled placement and subsequent synapse formation between different neural cell types. We also developed and characterized a new type of DNA-templated silver nanocluster that shows the remarkable ability to "light-up" when brought into close proximity with a guanine-rich oligonucleotide strand. This result is the basis of a new approach for DNA detection through a "nanocluster beacon" approach. In addition, multifunctional superparamagnetic iron platinum particles (SIPPs) were developed for use as magnetic resonance imaging (MRI) contrast agents and drug delivery vehicles for the targeted detection and therapy of prostate cancer. In the scientific theme area of new characterization tools, we have used spatially registered AFM and time-resolved single-particle fluorescence spectroscopy to study fluorescence intermittency and energy transfer in small clusters of quantum dots. We have also extended the capabilities of CINT's three-dimensional tracking microscope to enable the tracking of quantum-dot labeled antigens in a live cell. These studies follow both the motion of receptor-bound antigens on the cell membrane and subsequent endocytosis process, all with tens of nanometer precision. Highlights in the science area of exploring the roles of disorder and dynamics in controlling material performance include demonstration of the ability to prepare lipid membrane assemblies on nanoporous metal substrates where the lipid assemblies are both fluid and resistive. We have also used a combination of fluorescence spectroscopy, optical microscopy, and fluorescence lifetime measurements to characterize the nature of aggregates of conjugated oligomers, providing evidence for a core-shell-like structure consisting of loosely aggregated, monomer-like exterior and densely aggregated interior. Finally, the interaction of functionalized nanoparticles with lipid bilayer assemblies has been investigated as part of CINT's Integration Focus Activity on Membrane-Based Nanocomposites. Design rules have been established for predicting whether nanoparticles are adsorbed by, insert into, or are coated by lipid bilayers as a function of particle size, shape and surface chemistry.

As we move forward, we will continue our activities aimed at enabling integration science in the realm of soft and biological nanomaterial systems. Research in the area of controlling interfaces and interactions between disparate classes of materials will include collaborative work with researchers at LANSCE to apply neutron scattering methods to the study of DNA-templated Ag nanoclusters, establishment of thermodynamic size control in magnetite nanoparticles (as opposed to the standard kinetic control), further development of the Nanocluster Beacon concept and its use for assays such as single nucleotide polymorphism detection, and deployment of a capability for chemical vapor deposition growth of graphene sheets. Our efforts in developing and applying new characterization tools will include application of single-molecule imaging tools to improve the molecular level understanding cellulase activity, and demonstration of tracking of single green fluorescent proteins (GFPs) in three dimensions at rates comparable to intra-cellular trafficking processes. In the area of exploring the roles of disorder and dynamics in controlling material performance, we will work with CINT users to learn how to deploy programmable surfactant molecules into lipid bilayers as a means to program domain function, nanoparticle interactions with membranes, and membrane curvature in fluid lipid hosts. We will also extend the study of membranes on porous metal substrates to include the development and characterization of fluid lipid bilayers on nanoporous platinum substrates. We will demonstrate the controlled guidance of kinesin-microtubule molecular shuttles through manipulation and fluorescent tracking of attached Superparamagnetic Iron Oxide Nanoparticles (SPIONs). Finally, we will study the dynamic self-assembly of microtubule-nanoparticle composites to better understand the influence of elasto-mechanical forces that are involved in this process.



CINT Scientist highlight - Dale Huber

To materials chemist Dale Huber, most people remain unaware they have cancer precisely when the knowledge could help them most: when the number of harmfully mutating cells are treatably small. But in a kind of catch-22, Dale says, when the number of mutant cells are still trivial, they fall below the detection threshold of current sensors. So when preventive action would be easiest, nothing is done. "For example, mammography has a long history of not working well enough for early cancer detection," Dale says. "The tumor has to be big and obvious. The radiologist has to be able to read it in the image."
Improving early detection of cancerous cells is a particularly poignant problem when it comes to children, Dale says. "Leukemia is the number one childhood cancer. Even successfully treating it can knock as many as 20 IQ points off a developing child, according to some published studies."

To help improve early detection capabilities, Dale has left his comfort zone of (as he puts it) "squishy soft polymers" and instead is working with iron oxide nanoparticles in the Sandia/Los Alamos national laboratories joint Center for Integrated Nanotechnologies, where he is a Principal Member of the technical staff. (CINT is sponsored by DOE's Basic Energy Sciences office.) Providing technical backup in an approved "user" project to retired LANL researcher Ed Flynn and his company Senior Scientific LLC, Dale uses CINT technologies to help grow iron oxide nanoparticles twenty to thirty nanometers in diameter that ride antigens designed to hone in on the cells of a particular cancer.

Antigens that locate cancerous cells bind to those cells' receptors, stabilizing their magnetic riders. Those antigens which locate no cancers go whirling off harmlessly, essentially lost in space (or rather, the bloodstream), iron oxide nanoparticles destabilized. By subjecting the patient to a magnetic field that lasts three-tenths of a second, a clear signal is yielded by those nanoparticles attached to a stable base. Those unattached to a cancerous cell are rotated by random motion in a way that cancels any response. Thus, a signal is provided only from those iron oxide particles attached to cancerous cells. The beauty of the system is that even cancer distributed throughout the body can be detected. The new system shows their location clearly.

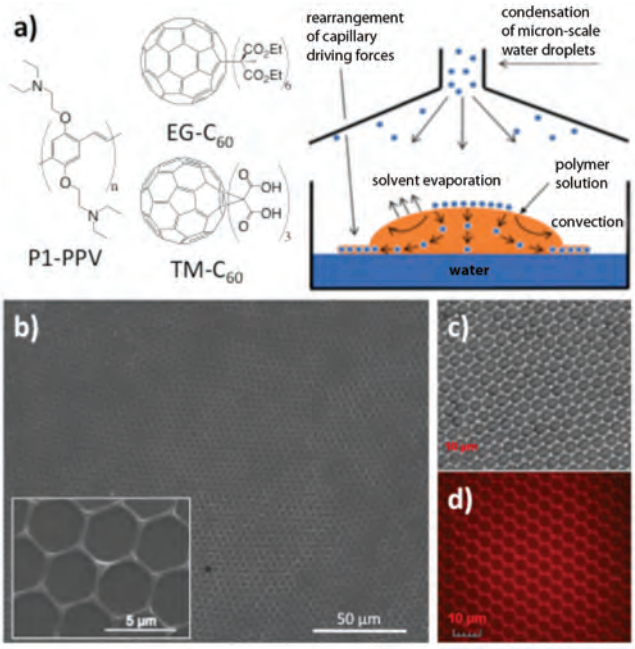
"Death comes when the number of cancer cells in the body reach, roughly, 10 to the 12th power," Dale says. "At 10 to the 9th power, the cancer is palpable. X-rays can detect cancers in amounts 10 to the 8th power. Our method, with its unambiguous signal, can detect it at 10 to the 4th power, literally doubling the time to treat the cancer." Additional treatments, he says, should greatly improve survival rates from microtumors. The interesting technique also could work to locate Alzheimers sites in the brain, he says. The antigen would be designed to attach to protein plaque called amyloids that haven't folded properly — a key indication of the presence of the disease. The same iron oxide particles in a similar magnetic field should reveal pools of disease, no matter how small. "We haven't done it because we lack the patience to wait till laboratory mice get Alzheimer's," he gently jokes.

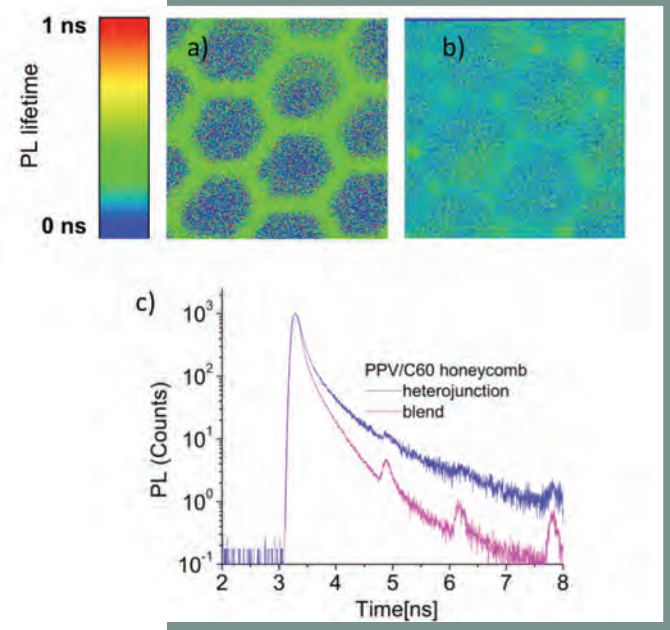
The ability to achieve iron nanoparticles of narrow size distribution, so that all particles have the same magnetic response, is one reason for the work's success to date, says Dale. "If the iron particles nucleate slowly and then grow, there's no catching up for the ones that nucleate later: they'll always be smaller than the ones that nucleated earlier. So we want, and have achieved in this system, rapid nucleation and slow growth." The science is an interesting change for a polymer chemist used to working with materials that grow like microscopic snakes, forming slowly yet growing to the same size. "I do a lot of different work I wouldn't have done without outside suggestion," says Dale. "Anyone can write a proposal to work with me; I welcome the chance to use CINT's capabilities to complete the technical cores of outside projects that matter deeply." A formal process is available for interested researchers to apply to work with CINT personnel and available CINT equipment. Federal agency approval will be required before testing the magnetic sensing technique in humans.

Patterned Assemblies of Fullerene-polymer Composites

Scientific Accomplishment:

Ordered porous frameworks of polymers are useful for a number of optical and electronic applications. The use of scalable self-assembly methods to produce such materials is of tremendous interest, in particular for the ability to produce inexpensive patterned films that may be used, for example, in solar energy production. CINT users and staff, working collaboratively with colleagues at the Center for Functional Nanomaterials at Brookhaven National Laboratory, have developed a method of producing patterned thin-film composites of functionalized conjugated polymers and fullerenes. These blends, patterned using the breath figure technique, have been characterized using optical and electron microscopy as well as fluorescence lifetime imaging microscopy. For appropriately functionalized and blended materials, the results demonstrate the presence of efficient photo-induced charge separation between the conjugated polymer and fullerene components. The patterning leads to an overall highly transparent film, with active optical absorption confined to the framework of the hexagonal structure.





(Left) (a) Structures of conjugated polymer and two types of functionalized fullerenes, along with a schematic of the breath-figure method used to produce patterned thin films. (b) SEM image (and zoom) of a pure polymer film. (c) Optical bright field and (d) fluorescence images of the polymer film deposited on a cover slip. (Right) Confocal fluorescence lifetime images of (a) polymer/fullerene heterjunction and (b) polymer/fullerene blend, with (c) corresponding lifetime traces.

Significance:

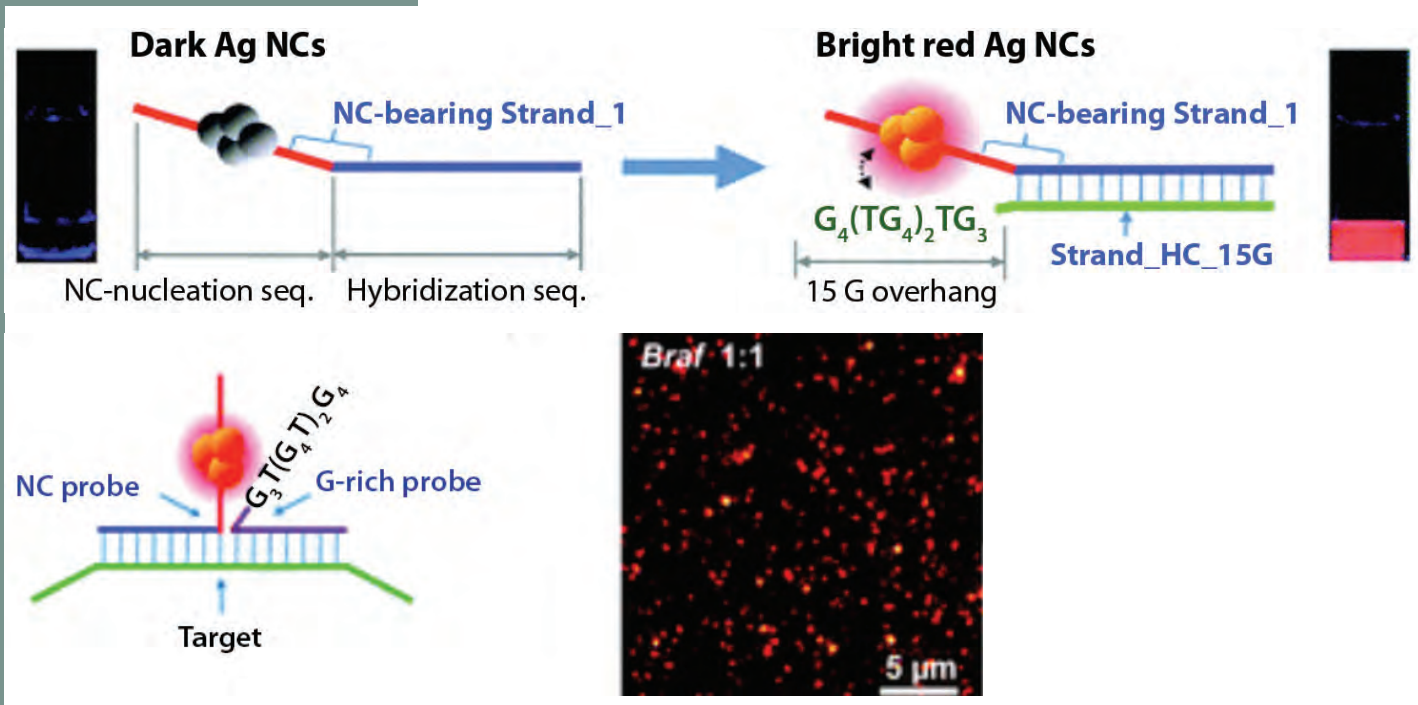
These materials demonstrate the use of solution self-assembly methods to produce active soft-material composites ordered across macroscopic length scales. Chemical functionalization of the components allows for control of their interactions, leading to materials with controlled multi-scale order and dynamics.

CINT Contact: *Andrew Dattelbaum*
User proposal U2008A169.
Publication:H.H. Tsai, Z. Xu, R.K. Pai, L.Y. Wang, A.M. Dattelbaum, A.P. Shreve, H.-L. Wang and M. Cotlet, "Structural dynamics and charge transfer via complexation with fullerene in large area conjugated polymer honeycomb thin films," Chem. Mater. (2010) in press.

Nanocluster Beacons

Scientific Accomplishment:

The development of new nanomaterials with biological applications is an area of substantial importance. One significant application is the detection of biological compounds with high sensitivity and specificity. For example, the detection of strands of DNA with sequence specificity is of tremendous importance in a variety of diagnostic and therapeutic settings. Current state-of-the-art technology for such detection relies on the use of so-called Molecular Beacons, which are hairpin-shaped nucleic acid probes that fluoresce upon hybridization with specific nucleic acid targets. However, Molecular Beacons suffer from some limitations including background due to imperfect fluorescence quenching in the "dark" state, the need for multiple labeling and associated purification steps, and the reliance on organic dye molecules susceptible to photobleaching.



(Top) A schematic and pictures of fluorescence emission showing how proximity to a guanine-rich strand leads to dramatic increase of the red emission from a DNA-templated silver nanocluster.
(Bottom) Fluorescence image taken at CINT showing individual Nanocluster Beacons bound with a genetic target.

To improve upon this existing technology, users and CINT researchers have developed a new class of probe materials based on Nanocluster Beacons. These probes rely upon noble-metal nanoclusters as the active species. In one implementation silver nanoclusters, consisting of just a few atoms of silver, are prepared using single-stranded DNA templates. The as-prepared clusters are not fluorescent, but fluorescence is activated when the cluster is brought into close proximity with a guanine-rich region of DNA. Thus, by attaching probe sequences to both the templating strand and a guanine-rich strand, one can detect the presence of a DNA sequence that is complementary to both probe sequences by the turn on of fluorescence emission from the cluster. In practice, the turn-on ratio can be as large as 500x, greatly exceeding the performance of existing detection strategies.

Significance:

The development of biologically templated synthetic nanomaterials for DNA detection and analysis is an example of how integration of biological and non-biological materials can lead to substantial improvement in macro-scale assays. The new methods developed here are a tremendous improvement on existing strategies based on more conventional organic fluorescent molecules, and illustrate the power of improved control of the interface between biological and non-biological systems.

CINT Contacts: *Jen Martinez, Jim Werner*

User Proposal: U2010A916

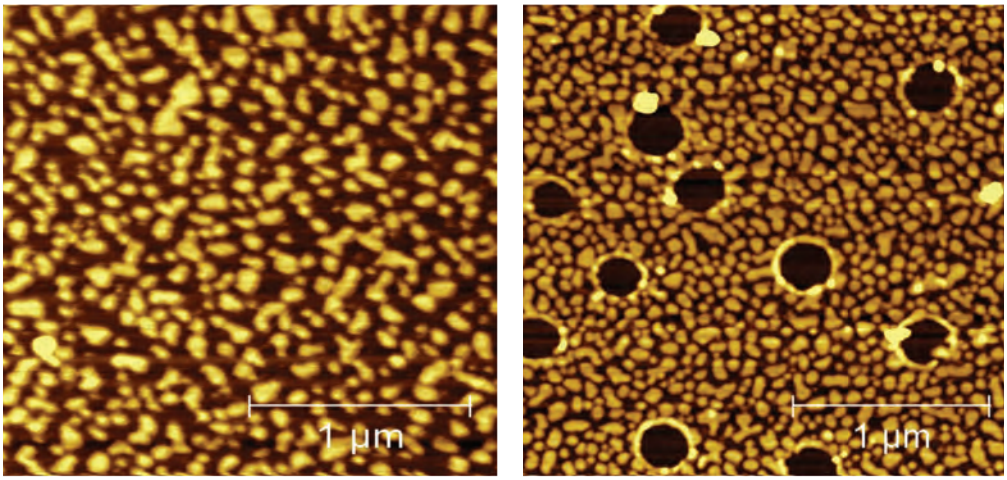
H.C. Yeh, J. Sharma, J.J. Han, J.S. Martinez and J.H. Werner, "A DNA-silver nanocluster probe that fluoresces upon hybridization," Nano Letters 10 (2010) 3106.

U.S. Provisional Patent Application, 2010.

Membrane-nanoparticle Composites

Scientific Accomplishment:

The interaction of synthetic nanoparticles with biological membranes is an area of substantial interest, both for understanding the response of biological systems to nanoparticle exposure and for material development methods that could lead to adaptive and responsive composite systems. To understand and control such interactions, several approaches have been explored. These include particle synthesis and chemical functionalization, characterization of the interaction of nanoparticles with model membrane assemblies, development of new types of substrate-supported model membrane assemblies, and study of the dynamics of membrane-particle composites. This work has led to the development and testing of design rules that govern the interaction of nanoparticles with various types of membrane assemblies. From such rules, one can understand the disposition of particles into the hydrophobic membrane interior, association of particles with hydrophilic membrane head groups, or the lack of any particle-membrane interaction.



(Left) An example of functionalized gold nanoparticles interacting with a phospholipid-based substrate-supported membrane. (Right) Upon exposure to zirconium salt, the entire membrane-particle assembly dynamically reconfigures to form nanoscale structures. Related studies have also explored the formation of vesicles at surfaces, the removal of lipids from surfaces by nanoparticles, and the controlled agglomeration of lipid-functionalized nanomaterials.

Significance:

A major challenge in nanoscale materials is development of structures that can mimic many of the functional properties of living systems. Such structures need to be responsive to their environment, adaptive and reconfigurable. The integration of synthetic nanomaterials with biological architectures such as lipid-membrane assemblies is a promising route toward the development of composite materials with these types of dynamic behavior. Systematic studies are beginning to show how such integration can be predictably and reliably controlled for a variety of particles and membrane types.

CINT Contacts: *Bruce Bunker, Gabe Montano*

CINT Science

M.P. Goertz, N. Goyal, B.C. Bunker and G.A. Montaño, "Substrate effects on interactions of lipid bilayer assemblies with bound nanoparticles," (2010) submitted.

M.P. Goertz, N. Goyal, B.C. Bunker and G.A. Montaño, "Lipid bilayer reorganization under extreme pH conditions," (2010) submitted.

Nanophotonics and Optical Nanomaterials

The Nanophotonics and Optical Nanomaterials thrust seeks to address the overall scientific challenge of understanding and controlling fundamental photonic, electronic and magnetic interactions in nanostructured optical materials fabricated using both chemical and physical synthesis. Major thrust research areas include: 1) Chemical and Physical Synthesis of Optical Low-Dimensional Nanophotonic Structures; 2) Optical Spectroscopy of Low-Dimensional Nanostructures; 3) Photonic Crystals, Metamaterials and Nanoplasmonics. This thrust interacts directly with the other three CINT scientific thrusts to leverage expertise in related fields such as theoretical analysis of nanostructures, soft biomaterials, ultrafast spectroscopy of hard and soft nanomaterials, and cleanroom semiconductor fabrication and processing. The scientific directions for this thrust will follow these three main categories and developments in these areas are expected to lead to rapid advances in light-capture applications (photovoltaics, photodetection, and radiation detection), light-emission applications (solid-state lighting, light-emitting diodes, lasers, etc.) and new understanding of electromagnetic phenomena and solid state excitations at the nanoscale.

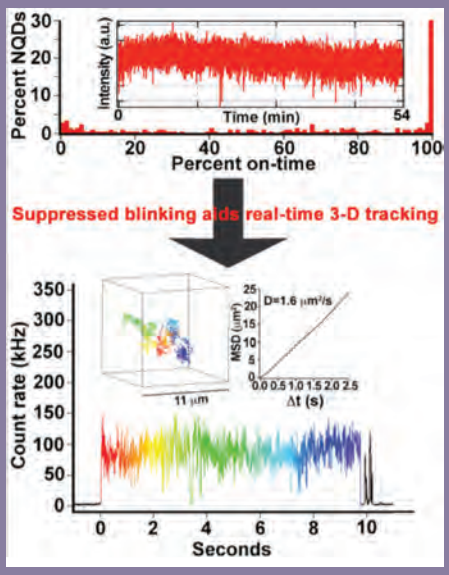
Significant progress has been made in the past year in support of user projects and internal science in the areas of metamaterials, semiconductor and carbon nanostructures (quantum dots, nanowires and tubes, and hybrid materials) for photonic and plasmonic applications, and new synthetic and characterization capabilities. Metamaterials work has focused on design, fabrication, and characterization of novel metamaterials including incorporation of tunable response functionality and extension of resonant frequencies into the thermal infrared region. Efforts in photonics include new applications for quantum dots, characterization of excited-state carrier dynamics, and ultrafast studies of emergent behavior in functional nanomaterials. New and/or improved synthetic protocols have been developed for core-shell quantum dots, solution-based routes to nanowires, and novel functional composites. New characterization capabilities include optical and electrical probes of individual nanostructures and their interfacial environments, time-resolved probes of carrier dynamics in these nanostructured materials and spectral ellipsometry for optical materials characterization

Specific accomplishments in the past year in metamaterials research include development of a novel approach for antireflection coatings using planar metamaterials in the terahertz frequency range, demonstration of thermally tunable high-temperature superconducting terahertz metamaterials including the resonance strength and frequency, and demonstration of doping tunable metamaterials in the thermal IR resulting in higher frequencies than all previous work done at THz frequencies. Highlights of our efforts in photonics include demonstration of giant QDs as light-emitting diodes with performance rivaling state of the art all inorganic NQD LEDs, advanced optical spectroscopy studies on individual semiconductor-metal hybrid nanostructures demonstrating plasmon-exciton coupling in multi-exciton regime, and several experimental firsts including the first observation of the relativistic nature of photoexcited quasiparticles in graphene and the first ultrafast optical experiments on single Si and GaN NWs. Notable advances in our synthetic efforts included development of new QD synthetic methods for non-cadmium-containing heterostructured QDs exhibiting significantly suppressed blinking and initial control over core/shell QD electronic structure by manipulation of core/shell interfaces, establishiment of unique solution-based capability for the synthesis of hybrid metal/semiconductor NWs with flexibility in choice of metal and semiconductor materials, and demonstration of the fabrication of dense, vertical arrays of II-VI semiconductor nanowires using a novel flow-reactor system. Highlights in the realm of capability development include establishment of electrochemistry and spectroelectrochemistry capabilities for characterization and manipulation of individual nanocrystalline materials and their environments, establishment of capacitance photocurrent spectroscopy and scanning photocurrent microscopy capabilities to investigate photo-generated carriers in semiconductor nanowires, and demonstration of a correlated TEM-Raman spectroscopy capability on individual Ge/Si core /shell nanowires.

Efforts in the coming year will continue in all these areas and build on these exciting accomplishments. In metamaterials research we plan to develop a high power terahertz system with low temperature capability suitable for investigation of our planned push into nonlinear metamaterials and further advance optical frequency tunable metamaterials through integration with bandgap enigineered transitions in semiconductoir heterostructures. The interaction between optical nanoparticles and nanoplasmonic structures will be studied through the integration of optical metamaterials and plasmonic resonators and waveguides with visible and infrared quantum dots. Research in other areas of photonic materials and properties will include development of an optical

near-field probe using loop waveguide for studying surface modes of nano-photonic structures, Raman measurements aimed at probing the origins of non-Condon effects in carbon nanotubes, exploration of the geometry dependence of SERS response from plasmonic particles, and use of THz time-domain spectroscopy to study the integer quantum Hall effect in two-dimensional electron gases, potentially extending these measurements to graphene. Our synthetic efforts will be extended to include development of bioconjugation strategies for integrating giant QDs into 3-D, single-molecule tracking experiments in live cells, and establishment of a new solution-phase synthetic methods for axially, radially and branched heterostructured NWs for enhanced functional properties for light emission and energy harvesting, and to facilitate integration into device structures. Capability development will continue to be a focus with new or advanced efforts including integration of photo-current imaging and spectroscopy with advanced single nanostructure optical spectroscopy techniques (PL, Raman and TRPL) use of the newly developed technique of ultrafast optical photography to image carrier dynamics in systems neurons to nanowires, and reducing the size limits of the electron beam lithography system and fabrication techniques at CINT to achieve yet smaller dimensionalities for use in, e.g., extending functionality from the infrared to visible wavelength regime.

Novel "Giant" Nanocrystal Quantum Dots for Applications in Advanced Bioimaging and Solid-state Lighting



Top "on-time" histogram of CdSe/19CdS g-NQD population constructed from analysis of typically >100 g-NQDs (single-g-NQD fluorescence time trace shown as inset) translates to practical effect in the bottom 3-D fluorescence intensity trajectory of a single g-NQD diffusing in a viscous aqueous solution.

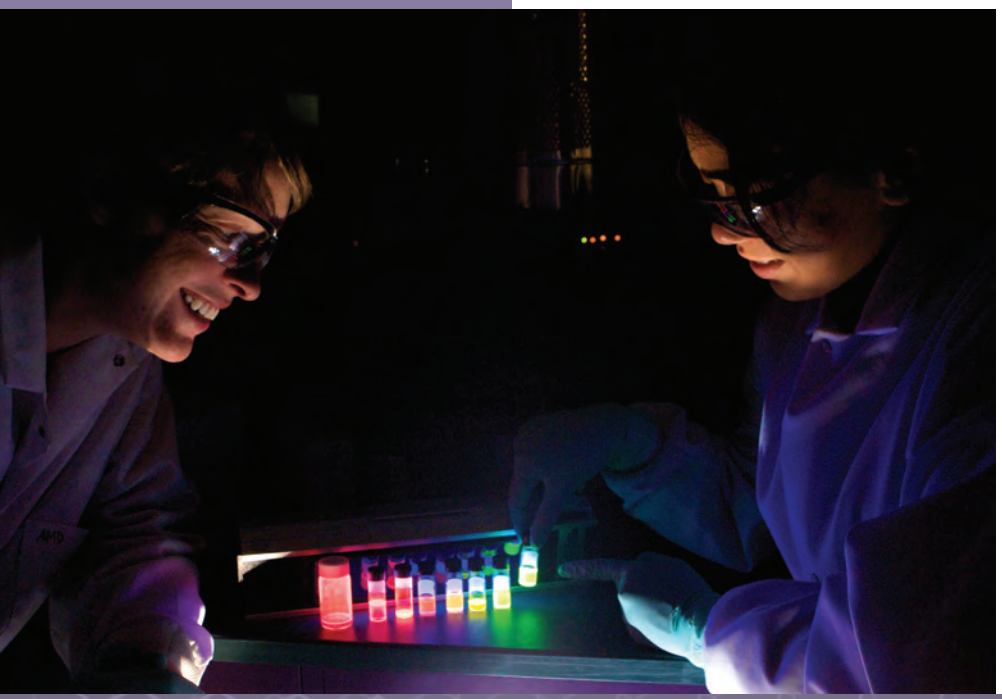
CINT Contact: Jennifer Hollingsworth

User Proposals: U2008A109 and U2008A078.
J. Vela, et al. Effect of shell thickness and composition on blinking suppression and the blinking mechanism in 'giant' CdSe/CdS nanocrystal quantum dots, J. Biophoton. 2010, 3, 706-717.
H. Htoon, et al, Highly Emissive Multiexcitons in Steady-State Photoluminescence of Individual "Giant" CdSe/CdS Core/Shell Nanocrystals, Nano Lett. 2010, 10, 2401-2407.

Scientific Accomplishments:

Nanocrystal quantum dots (NQDs) are semiconductor nanoparticles with remarkable size-tunable optical properties, including the ability to emit light efficiently when optically excited, with enhanced stability compared to molecular dye fluorophores. Furthermore, for NQDs, emission "colors" are tunable as a simple function of particle size and composition, and NQDs are conveniently chemically manipulated for both solution-phase and solid-state purposes. Despite these inherent advantages, NQD application potential has been limited due to a once seemingly inherent property known as fluorescence intermittency, or "blinking" – under continuous illumination, single NQDs can be seen to turn "on" and "off" in an unpredictable fashion. Blinking limits the utility of conventional NQDs for applications requiring continuous and reliable emission of photons, such as single-particle tracking in advanced bioimaging and as single-photon light sources in quantum cryptography. In addition, NQDs are characterized by an efficient nonradiative carrier recombination process known as Auger recombination, which prevents efficient generation of light under charged or multiply excited conditions.

Recently, we developed an inorganic shell approach for suppressing blinking in NQDs that for the first time revealed a reliable path forward for eliminating this debilitating NQD property (Chen et al. J. Am. Chem. Soc. 2008). By applying an ultrathick and structurally perfect shell of a higher bandgap semiconductor to the core NQD, we established a new class of NQD, the so-called "giant" NQD (g-NQD) characterized by suppressed blinking and remarkable photostability. Critical for applications that require balancing performance enhancement with minimizing particle size, e.g., applications in biological imaging and tracking, we showed that depending on experimental requirements, e.g., time-of-use needs, relatively thinner shell (smaller) g-NQDs might be perfectly adequate, while the thickest shell systems remain key for the most demanding of applications. As a proof-of-principle of their utility for single-particle tracking in biologically relevant environments, we showed that g-NQDs outperform commercial NQDs in three-dimensional tracking experiments. Finally, we demonstrated that strong emission from both neutral and charged biexcitons, as well as multiexcitons of higher order, points toward a significant suppression of nonradiative Auger recombination that normally renders multiexcitons nonemissive.



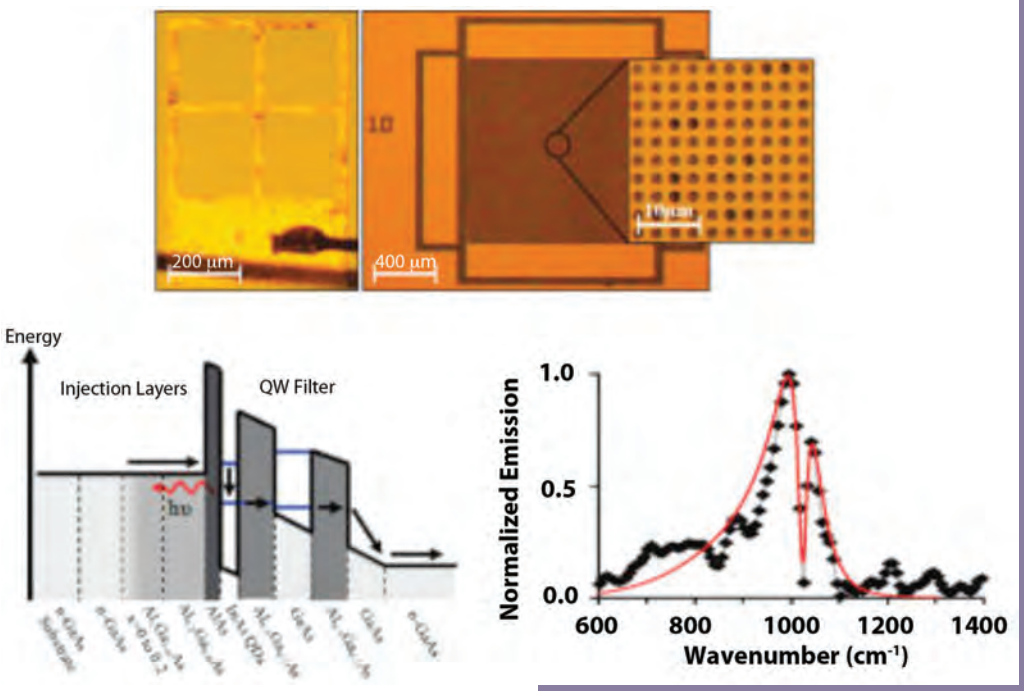
Significance:

To a large extent, our new NQD architecture—the "g-NQD"—solves the key issues associated with conventional NQDs for applications in advanced bioimaging and efficient, stable light emission (e.g., solid-state lighting, lasing, single-photon sources). The science and new application potential afforded by these optical nanomaterials cut across multiple CINT Thrusts, especially Nanophotonics & Optical Nanomaterials (nanoscale control of energy transformations), Soft, Biological & Composite Nanomaterials (new fluorophores for single-molecule spectroscopy), Theory & Simulation of Nanoscale Phenomena (interfacial interactions and emergent properties).

Rabi Splitting from Surface Plasmon Coupled Conduction State Transitions in InAs Quantum Dots

Scientific Accomplishment:

Rabi oscillations underlie all light-matter interactions involving coherent transients, quantum interference, and (in the case of vacuum Rabi oscillations) cavity quantum electrodynamics. To date Rabi oscillation has been demonstrated by optically exciting nanostructures embedded in microcavities, organic semiconductor microcavities, organic molecules interacting with surface plasmons (SPs), SP coupled CdSe nanocrystals, and electrically injected polariton microcavity light-emitting diodes and intersubband devices. We now report strong coupling in electrically excited semiconductor nanostructures. The experiments were performed on mid-infrared (mid-IR) emitting quantum-cascadelike structures utilizing self-assembled InAs quantum dots (QDs) in the device active region, whose intersublevel transitions are coupled to SP excitations. We demonstrate strong coupling between a surface plasmon and intersublevel transitions in self-assembled InAs quantum dots. The surface plasmon mode exists at the interface between the semiconductor emitter structure and a periodic array of holes perforating a metallic Pd/Ge/Au film that also serves as the top electrical contact for the emitters. Spectrally narrowed quantum-dot electroluminescence was observed for devices with varying subwavelength hole spacing. Devices designed for 9, 10, and 11 μm wavelength emission also exhibit a significant spectral splitting. The association of the splitting with quantum-dot Rabi oscillation is consistent with results from a calculation of spontaneous emission from an interacting plasmonic field and quantum-dot ensemble. The fact that this Rabi oscillation can be observed in an incoherently excited, highly inhomogeneously broadened system demonstrates the utility of intersublevel transitions in quantum dots for investigations of coherent transient and quantum coherence phenomena.



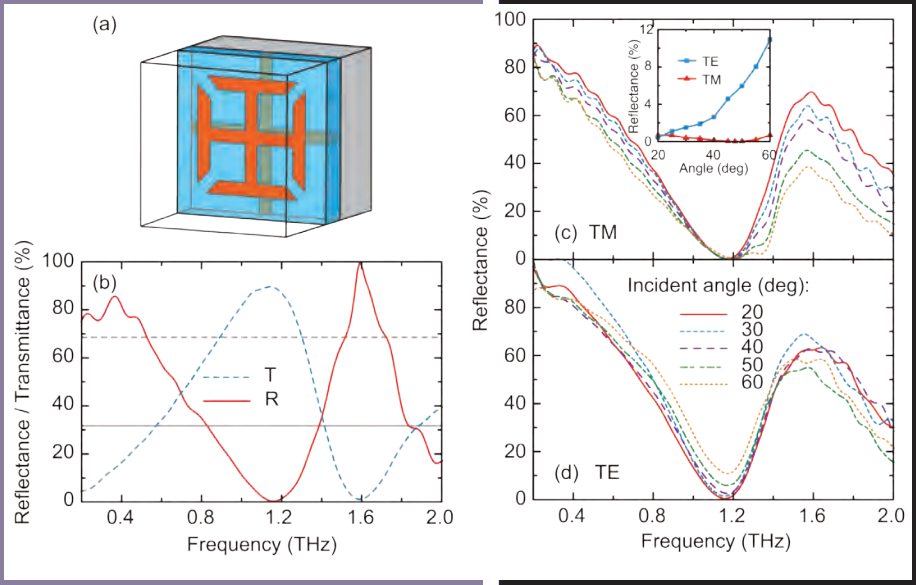
Top: QD device geometry for window contact (left) and mesh device (right). Bottom: (left) Electron confinement potential along the growth direction. This arrangement pushes the QD ground state energy above the GaAs band edge. (right) Electroluminescence spectrum of a 10 mm mesh-contact device. Black dots and connecting line are experimental data and the red curve is from theory.

Significance:

The observation of Rabi oscillations signals a strong coupling between radiation and an active medium that can lead to new functionalities in devices. Examples include the feasibility of laser action at X-ray or even γ-ray wavelengths, the development of nonclassical light sources, and the capability for fast, sensitive detection of biochemical agents using femtosecond adaptive spectroscopic techniques applied to coherent anti-Stokes Raman spectroscopy. The observation of Rabi oscillation or strong coupling in a semiconductor system is particularly significant. On the one hand is the interesting physics arising from reproducing the atomic light-matter interaction effects in a physically more complex many-body environment. On the other hand is the considerable application potential, because of the widespread use of optoelectronic devices in our daily lives.

CINT Contact: Igal Brener
User Project C2010A962
B. S. Passmore, D. C. Adams, T. Ribaudo, D. Wasserman, S. Lyon, P. Davids, W. W. Chow, and E. A. Shaner, "Observation of Rabi Splitting from Surface Plasmon Coupled Conduction State Transitions in Electrically Excited InAs Quantum Dots," NanoLetters 11, 338 (2011).

Antireflection Coating using Metamaterials & Identification of its Mechanism

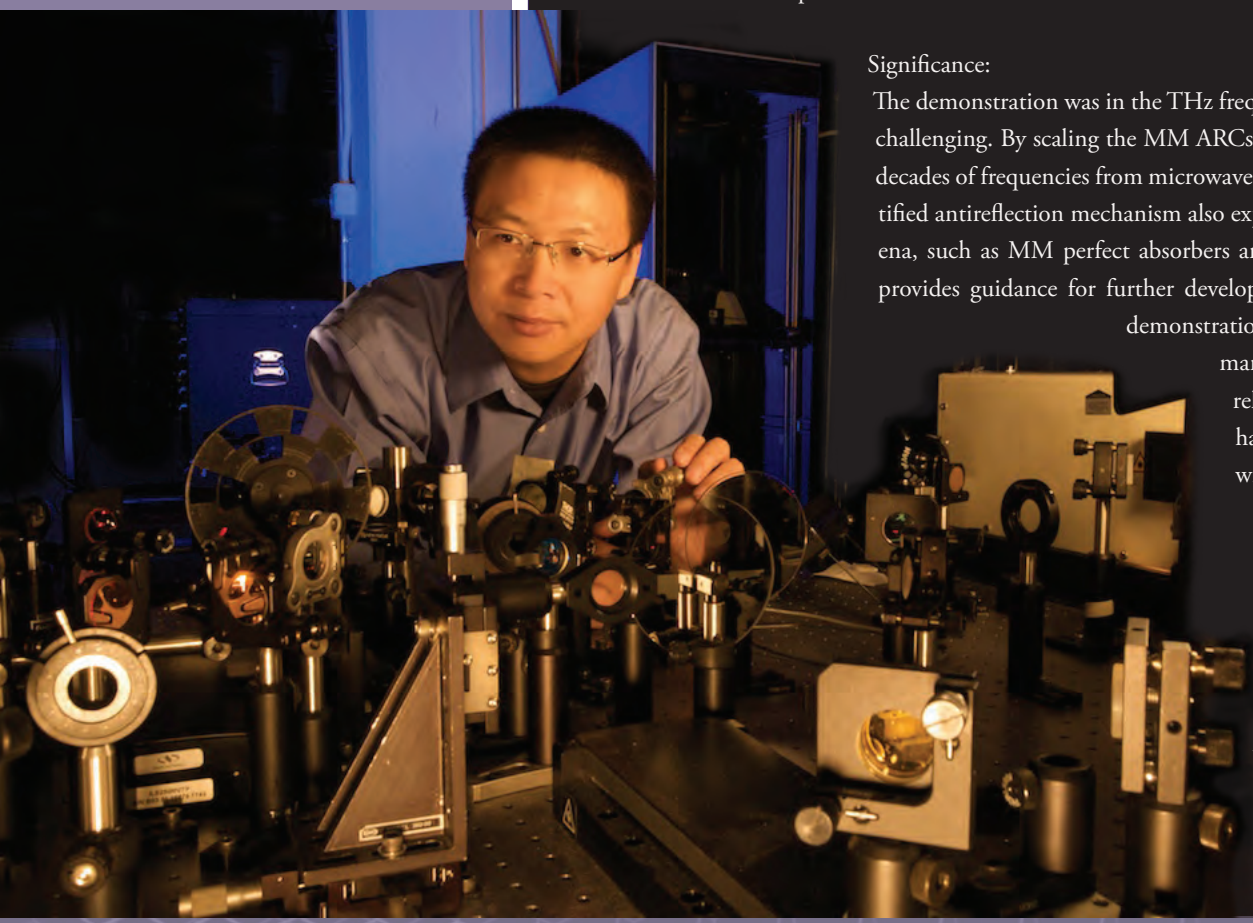


(a) Schematic design of one unit cell of the MM ARC. (b) Experimentally measured reflectance and transmittance under normal incidence. The angular dependence of reflectance spectra are shown for (c) TM and (d) TE polarized incident THz radiation. Inset: Angular dependent reflectance at the antireflection frequency.

Scientific Accomplishment:

When propagating electromagnetic (EM) waves encounter an interface of two media with different refractive indices, some portion of energy is reflected back, and the rest is transmitted through. This well-known phenomenon is the basis of numerous optical technologies. However, in many applications, reflection has adverse effects in an optical system and is therefore undesirable. Antireflection coatings (ARCs) are of additional importance to increase the throughput when considering the generally low power in many terahertz (THz) systems, where conventional ARC technology is limited by the availability of coating materials and the challenges in fabricating high-quality and relatively thick films.

Metamaterials (MMs) provide new opportunities to realize alternative ARCs by overcoming these limitations with engineered material properties. We demonstrated MM ARCs that are capable of dramatic reduction of reflection and great enhancement of transmission near a specifically designed frequency. They operate over a wide range of incidence angles and are polarization independent, i.e., working for both transverse magnetic (TM) and transverse electric (TE) polarizations. In principle, the demonstration could be applied to substrate materials with any value of dielectric constant, and the overall coating is of extreme subwavelength thickness. We further identified an interference mechanism that is responsible for the MM ARC, in contrast to the conventional understanding.



Significance:

The demonstration was in the THz frequency range where ARCs are challenging. By scaling the MM ARCs can be translated over many decades of frequencies from microwave to optical regimes. The identified antireflection mechanism also explains other related phenomena, such as MM perfect absorbers and EM wave tunneling, and provides guidance for further development of MM devices. This demonstration could be integrated into many THz systems and is also relevant in developing energy harvesting nano MM devices with improved performance.

CINT Contact: *HouTong Chen*

CINT Science Publication: H.-T. Chen, J. Zhou, J. F. O'Hara, F. Chen, A. K. Azad, and A. J. Taylor, "Antireflection coating using metamaterials and identification of its mechanism," Physical Review Letters 105, 073901 (2010).

Theory & Simulation of Nanoscale Phenomena

The Theory and Simulation of Nanoscale Phenomena Thrust focuses on identifying the fundamental concepts that control the behavior of integrated materials and systems with nanoscale structure. As the relative strengths of various interactions change with length scale, competition between interactions can lead to spontaneous self-organization at characteristic length scales. In integrated nanosystems, these intrinsic length scales can couple to naturally occurring or artificially imposed nanoscale inhomogeneity leading to the coexistence of different types of ordering and/or emergent phenomena. The various components of an integrated nanosystem each have their own intrinsic properties. This provides freedom to control and optimize system behavior. Conversely, successful nanoscale integration requires control over the interactions between components, which must be weak enough to maintain the unique properties of the nanoscale components, but strong enough that the components interact in order to achieve new properties and functionality. Improved understanding of how the interactions in nanosystems can be controlled through integration and how novel behavior emerges as a result of integration will help optimize particular functionality and even achieve multifunctional and/or responsive materials and systems. Therefore, this Thrust aims to understand the role of novel and competing interactions in nanoscale integration. This effort is organized into three science directions that together form the basis for integration at the nanoscale: (i) Nanoparticles in Complex Environments, (ii) Excitation and Transport in Nanostructured Systems, and (iii) Nanodomain/Nanostructure Interactions.

Work in the past year in collaboration with our user community has led to new theoretical and/or computational tools and capabilities as well as significant progress in each of our three science directions. In particular, our capability base has been expanded through the installation of a new CINT computer cluster (104 nodes, 912 CPUs, 5TB memory) that is currently online and available for CINT users. New theoretical and/or computational tools include development of a theory of localized plasmonic excitations in graphene, development of a theory of a Berry phase controlled Kondo effect in graphene, and development of a theory of competing superconducting-ferroelectric fluctuations at oxide interfaces. We continue to develop visualization capability in our thrust with recent applications to 3D GaAs k*p interactions, dislocation MD simulations. We also extended our Exciton Scattering Model (a novel theoretical method allowing us to simulate the excited state structure of macromolecular structures with thousands of atoms) for modeling UV-Vis absorption spectra. In studies focused on nanoparticles in complex environments, we used classical density functional theory calculations of three-body interactions among nanoparticles in a polymer melt to show that these interactions are thermodynamically significant. We also used molecular dynamics simulations to show that small nanoparticles with the relatively short dimensions of the coating can produce highly asymmetric coating arrangements both in solution and at liquid/vapor interfaces. In the area of excitation and transport in nanostructured systems, highlights include calculations of the electronic structure of realistically-sized, internally-strained heterogeneous nanowires and new properties of fully quantum electron-phonon coupled nanowire systems. Progress in the area of nanodomain / nanostructure interactions included demonstration using self-consistent PRISM theory that the chains in a melt polymer nanocomposite expand due to the addition of the nanoscale filler. We also calculated the effects of attractions on the surface-induced phase transition in polymer nanocomposites, finding that the phase transition changes from first to second order for sufficiently strong attractions, and we correlated the evolution of entanglements at a polymer interface to the mechanical strength and failure mode of polymer interfaces. Finally, we completed simulations of the interactions between neurofilament nanobrushes.

continued on page 40

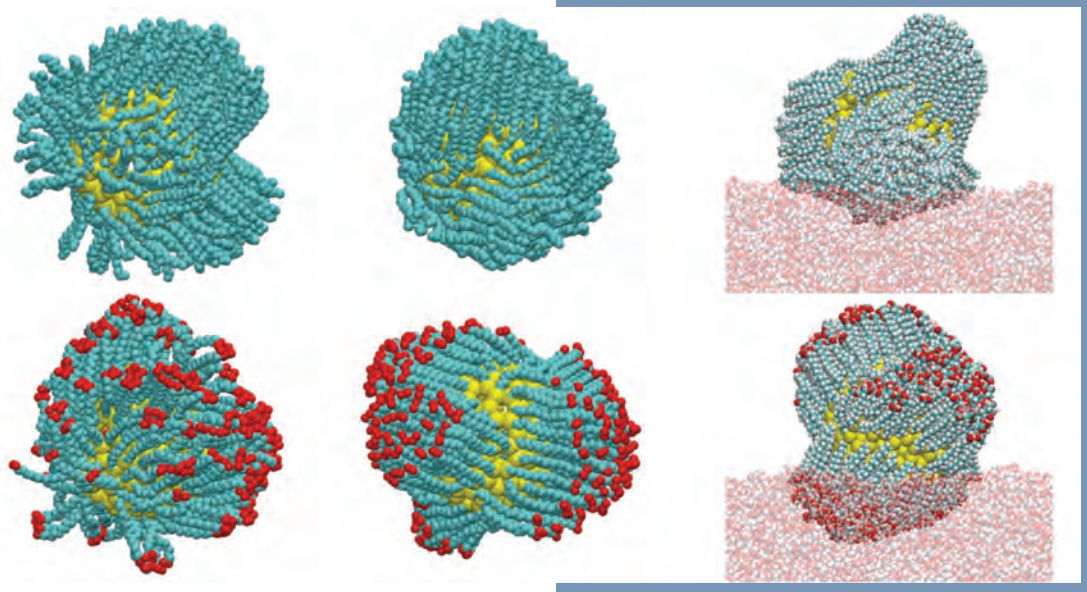
Theory & Simulation of Nanoscale Phenomena (continued)

In the coming year our efforts to understand nanoparticles in complex environments and nanodomain/nanostructure interfaces will include determining the phase behavior and effect of confinement on mixed polymer brushes using self-consistent field theory, calculating forces between polymer-coated nanorods to rationalize experimental results on the dispersion of coated rods in a homopolymer matrix, and studying interfacial behavior in polymer nanocomposites in more realistic model systems using classical density functional theory and MD simulations. We will also apply large scale atomistic molecular dynamic simulations to probe the molecular conformation of conjugated polymers confined to optically active nanoparticles, and study the diffusion of nanoparticles and proteins in a lipid bilayer. In the theme of excitation and transport, we will further develop our understanding of the effects of the Dirac spectrum on the magnetic screening and the Kondo effect in graphene and other Dirac materials, competing interactions at the interfaces and further develop our approach linking time-dependent density functional theory, classical molecular dynamics, and finite-element-based continuum simulations to study heat transport in nanostructures. We will continue studies of electronic structure and nonlinear optical response in hybrid organic/inorganic and organometallic structures for obtaining materials with desired functionalities, and conduct and model experiments involving ultrafast optical probes of multiferroic compounds. In addition, we will further expand our theory/simulation toolbox through continued development of efficient theoretical methods to study excited state structure and dynamics and to model electronic and optical spectroscopic probes at the nanoscale, and through development of the theory of inelastic scattering in nanoscale modulated states like stripes and atomic corrals.

Spontaneous Asymmetry of Coated Spherical Nanoparticles in Solution and at Liquid-Vapor Interfaces

Scientific Accomplishment:

Among the most prevalent ways to control the assembly and integration of nanoparticles is to coat their surfaces with organic molecules whose specific functionalized groups would modify the inter particle interactions as well as the interaction of nanoparticles with their surrounding, while retaining their inherent properties. While it is often assumed that uniformly coating spherical nanoparticles with short organics will lead to symmetric nanoparticles, we find that the high curvature of small nanoparticles and the relatively short dimensions of the coating can produce highly asymmetric coating arrangements. Using explicit-atom molecular dynamics simulations of model nanoparticles, we showed that in solution geometric properties dictate when a coating's spherical symmetry will be unstable and that the chain end group and the solvent play a secondary role in determining the properties of surface patterns. Importantly, we demonstrate that small particles cannot be fully encapsulated with coatings made of simple chains. This has implications in countless nanotechnology applications.



4 nm diameter Au nanoparticles with alkanethiol ligands S-(CH2)17-X with X=CH3 (top row) and COOH (bottom row) in decane (left) and water (middle) and at the water/vapor interface (right).

At the water-vapor interface, we find also that the anisotropic nanoparticle coatings seen in bulk solvents are reinforced by interactions at the interface. The coatings are significantly distorted and oriented by the surface as seen in the illustration below. The coating shape depends strongly on the amount of free volume provided by the geometry, end group, and solvent properties. Unlike in the bulk, at an interface any inhomogeneity or asymmetry tends to orient with the surface so as to minimize free energy.

Significance:

These asymmetric and oriented coatings are expected to have a dramatic effect on the interactions between nanoparticles and will surely influence the structures of aggregated nanoparticles which self-assemble in the bulk and at surfaces. This work is part of our effort to understand the interactions of nanoparticles in membranes.

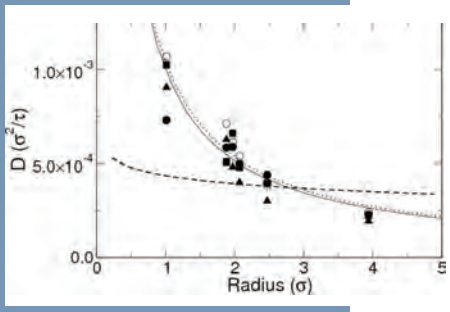
CINT Contact: *Gary Grest*
CINT Science

J. Matthew D. Lane and Gary S. Grest, Spontaneous Asymmetry of Coated Spherical Nanoparticles in Solution and at Liquid-Vapor Interfaces, Physical Review Letters 104, 235501 (2010); Cover June 11, 2010 issue Physical Review Letters; Featured in Sandia Lab News, vol. 62, no. 18, September 24, 2010.

Size Dependence of Diffusion in Lipid Bilayers

Scientific Accomplishment:

The standard theory for diffusion of inclusions (proteins or nanoparticles) in a lipid bilayer is the Saffman-Delbrück relation, which gives the diffusion rate as scaling as log R, where R is the protein radius. Some recent experimental data has found a 1/R dependence instead, and a new theoretical analysis has shown that 1/R scaling should occur under some conditions. We have investigated the diffusion of inclusions using molecular dynamics simulations of minimal models of lipids and cylindrical proteins. The minimal models maintain the self-assembly of the lipid bilayer due to the competition of the hydrophobic and hydrophilic components of the lipid. Overall the model contains more features than the models used to derived the analytic expressions for the diffusion. Our simulations have found that a 1/R dependence clearly fits the data better than the log R expression.



The protein diffusion coefficient calculated from the protein mobility is shown for lipids with tail length NT = 3 (filled triangles), NT = 4 (filled squares), and NT = 5 (filled circles). The lipid diffusion is calculated from the lipid mobility for NT = 3 (open triangle), NT = 4 (open square), NT = 5 (open circle). The 1/R model for NT = 4 is represented by the dotted lines, the Saffman-Delbück model is represented by the dashed lines, and the free area theory model is represented by the solid line.

Significance:

The diffusion of transmembrane proteins is a fundamental biophysical process. These dynamics underlie many biological processes including cell-cell signaling, the action of the some toxins, and the kinetics of viral entry into cells. Understanding the fundamental physics of this process will also apply to the understanding of the kinetics of artificial amphiphilic nanoparticles that embed themselves in lipid bilayers. As shown by the pioneering theoretical work of Saffman and Delbrück, the size-dependence of the diffusivity of membrane inclusions is rather subtle due to the viscous coupling of an effectively two-dimensional liquid in which they move (the membrane) to the surrounding solvent. They showed that membrane hydrodynamics of this form admits an inherent length scale set to the ratio of two-dimensional membrane viscosity to the normal viscosity of the surrounding solvents. In this way low Reynolds number flows are fundamentally different from traditional three-dimensional hydrodynamics. They calculated the mobility (and hence diffusivity) of embedded particles in the limit that their size is small compared to this length Saffmann-Delbrück length. Their results show that the diffusion constant of membrane inclusions are only weakly dependent on the size of the diffusing particle (log R, were R is the particle radius), when that size is small compared to the SD length. In contrast, the diffusion constant for objects in three-dimensional viscous liquids depends inversely on particle size for all sizes.

Levine et al. have shown in a recent calculation that one may account for the experimentally observed failure of the Saffman-Delbrück diffusivity of membrane bound proteins in a manner akin to the classical problem of polarons and electron mobility in crystals. The strong attractive interaction of hydrophobic residues of transmembrane proteins to the oily lipid tails generates a local deformation of either chain tilt or stretch in a boundary layer immediately surrounding the protein. By thus introducing new degrees of freedom of the membrane not considered originally, there will be enhanced dissipation as the moving protein carries this deformation around with it. This dissipation enhancement (and thus mobility decrease) scales with the area of this boundary layer, which in turn scales linearly with the linear dimension of the transmembrane protein. As long as the deformation in the boundary layer is strong enough so that the power dissipated in the membrane is at least comparable to the dissipation in the usual flows of the unperturbed membrane, one will observe an inverse radius dependence of the protein diffusivity as seen recently by Gambin et al.

CINT Contact: *Mark Stevens*
User Proposal: U2009A092 Protein and Nanoparticle Dynamics in Lipid Bilayers, in preparation.

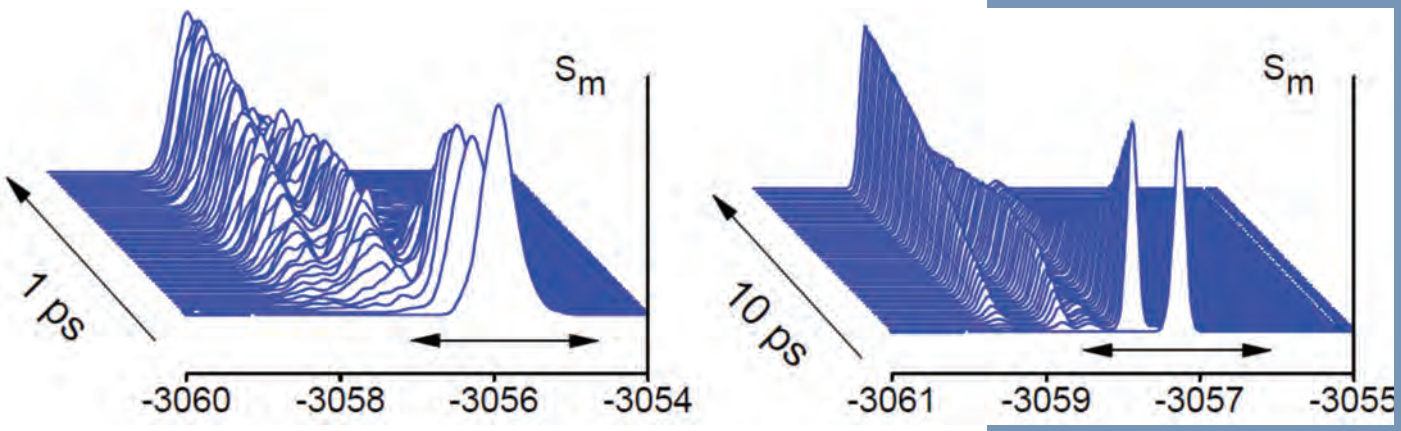
The NA-ESMD Modeling of Photoinduced Dynamics in Conjugated Molecules

Scientific Accomplishment:

Non-adiabatic dynamics generally defines the entire evolution of electronic excitations in optically active molecular materials. It is commonly associated with a number of fundamental and complex processes such as intraband relaxation, energy transfer and light-harvesting influenced by the spatial evolution of excitations, and transformation of photoexcitation energy into electrical energy via charge separation (e.g., charge injection at interfaces).

To treat ultrafast excited state dynamics and exciton/charge transport we have developed a non-adiabatic excited state molecular dynamics (NA-ESMD) framework incorporating quantum transitions. Our calculations rely on the use of the Collective Electronic Oscillator (CEO) package accounting for many-body effects and actual potential energy surfaces of the excited states combined with the Tully's fewest switches algorithm for surface hopping for probing non-adiabatic processes. This method is applied to model the photoinduced dynamics of distyrylbenzene (a small oligomer of polyphenylene vinylene, PPV). Our analysis shows intricate details of photoinduced vibronic relaxation and identifies specific slow and fast nuclear motions that are strongly coupled to the electronic degrees of freedom, namely torsion and bond length alternation, respectively. Non-adiabatic relaxation of the highly excited Sm state is predicted to occur on a femtosecond timescale at room temperature and on a picoseconds timescale at low temperature.

The wavepacket dynamics in an oligomer of polyphenylene vinylene (PPV) is constructed from energy histograms plotted at 20 fs (right side) and 200 fs (left side) intervals for T=300K and T=10K dynamics, respectively. The evolution of wavepacket mimicking pump-probe spectroscopy excitation from the ground state S0 to the highly excited state Sm is shown. The Sm wavepacket branches into three distinct peaks due to large gaps in the density of excited states.



Significance:

Understanding and control over photoinduced pathways lies at the heart of all our efforts to design functional photoactive materials for many technological applications (e.g., solar energy harvesting). Time-resolved ultrafast spectroscopy is a major tool to probe such dynamics on fs- to ns- timescales. Our developed computational tools are capable of modeling non-adiabatic excited state dynamics on ~10 ps timescales of large realistic molecules (hundreds of atoms in size) in the realistic dielectric environment, this capability provides the theoretical counterpart to experimental ultrafast spectroscopy, being able to treat the material on the same footing. We envision applications of this tool to a number of interesting molecular systems currently of focus in experimental research.

CINT Contact: *Sergei Tretiak*
User Proposal: C2009B011

T. Nelson, S. F. Alberti, V. Chernyak, A. Roitberg, S. Tretiak, The NA-ESMD Modeling of Photoinduced Dynamics in Conjugated Molecules, Journal of Physical Chemistry B, (2011) in press.

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Distinguished Affiliate Scientists

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Michael Nastasi (Los Alamos)
Darryl Smith (Los Alamos)
Antoinette Taylor (Los Alamos)

CINT Awards

Tom Picraux

- Chair and Retiring Chair of AAAS Section P (Industrial Science & Technology) 2009-2010

Sergei Tretiak

- Fellows Prize for Reseaerch, Los Alamos National Laboratory - 2010

Nate Mara

- Distinguished Mentor Perfomance Award--Los Alamos National Laboratory - 2010

Peter Goodwin

- Named Adjunct Professor, Physics and Astronomy Department, University of New Mexico - 2010

Shadi Dayeh

- Distingushed Postdoctoral Performance Award, Los Alamos National Laboratory - 2010

Amit Misra

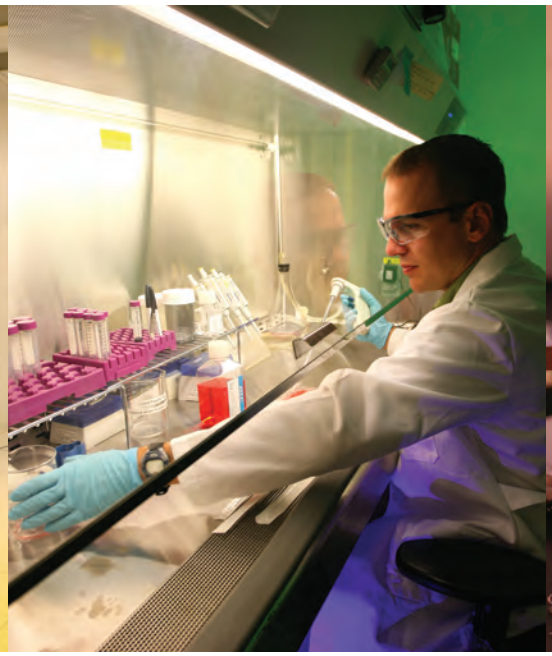
- Appointed permanent member of the Editorial Board of MRS Bulletin - 2010
- Distinguished Scientist/Engineer Award from the Materials Processing and Manufacturing Division (MPMD) of The Minerals, Metals and Materials Society (TMS) - 2011

Gary Grest

- Winner of the American Physical Society Polymer Physics Prize - 2011

Michael Nastasi

- Selected as a Materials Research Society (MRS) Fellow - 2011



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